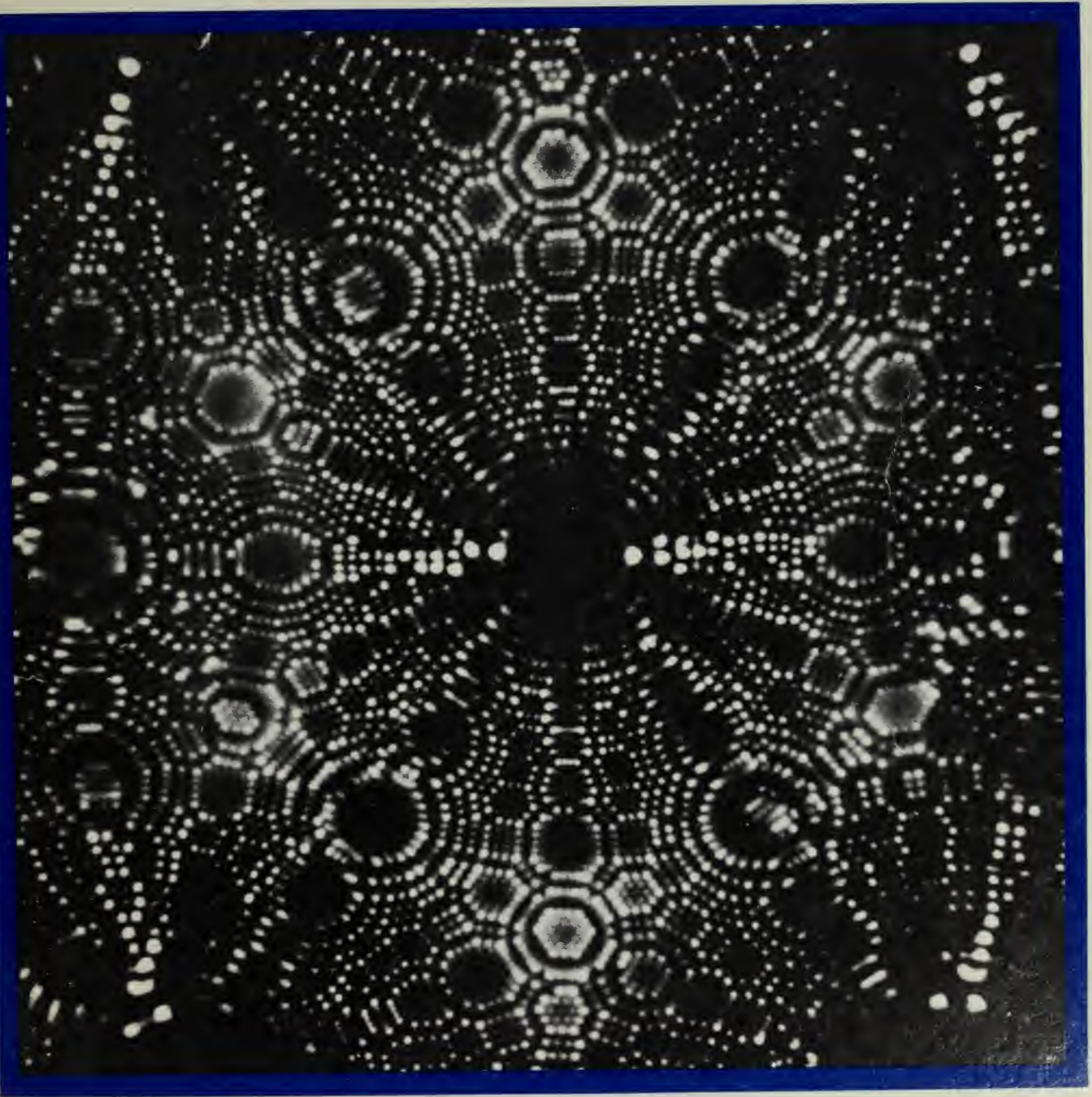


Models of the Atom



The Project Physics Course

Text and Handbook

UNIT **5** Models of the Atom

A Component of the
Project Physics Course



Published by
HOLT, RINEHART and WINSTON, Inc.
New York, Toronto

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This Text-Handbook, Unit 5 is one of the many instructional materials developed for the Project Physics Course. These materials include Texts, Handbooks, Teacher Resource Books, Readers, Programmed Instruction booklets, Film Loops, Transparencies, 16mm films, and laboratory equipment.

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The individuals listed below (and on the following pages) have each contributed in some way to the development of the course materials. Their periods of participation ranged from brief consultations to full-time involvement in the team for several years. The affiliations indicated are those just prior to or during the period of participation.

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(continued on p. 122)

Science is an adventure of the whole human race to learn to live in and perhaps to love the universe in which they are. To be a part of it is to understand, to understand oneself, to begin to feel that there is a capacity within man far beyond what he felt he had, of an infinite extension of human possibilities . . .

I propose that science be taught at whatever level, from the lowest to the highest, in the humanistic way. It should be taught with a certain historical understanding, with a certain philosophical understanding, with a social understanding and a human understanding in the sense of the biography, the nature of the people who made this construction, the triumphs, the trials, the tribulations.

I. I. RABI
Nobel Laureate in Physics

Preface

Background The Project Physics Course is based on the ideas and research of a national curriculum development project that worked in three phases. First, the authors—a high school physics teacher, a university physicist, and a professor of science education—collaborated to lay out the main goals and topics of a new introductory physics course. They worked together from 1962 to 1964 with financial support from the Carnegie Corporation of New York, and the first version of the text was tried out in two schools with encouraging results.

These preliminary results led to the second phase of the Project when a series of major grants were obtained from the U.S. Office of Education and the National Science Foundation, starting in 1964. Invaluable additional financial support was also provided by the Ford Foundation, the Alfred P. Sloan Foundation, the Carnegie Corporation, and Harvard University. A large number of collaborators were brought together from all parts of the nation, and the group worked together for over four years under the title *Harvard Project Physics*. At the Project's center, located at Harvard University, Cambridge, Massachusetts, the staff and consultants included college and high school physics teachers, astronomers, chemists, historians and philosophers of science, science educators, psychologists, evaluation specialists, engineers, film makers, artists and graphic designers. The teachers serving as field consultants and the students in the trial classes were also of vital importance to the success of Harvard Project Physics. As each successive experimental version of the course was developed, it was tried out in schools throughout the United States and Canada. The teachers and students in those schools reported their criticisms and suggestions to the staff in Cambridge, and these reports became the basis for the subsequent revisions of the course materials. In the Preface to Unit 1 *Text* you will find a list of the major aims of the course.

We wish it were possible to list in detail the contributions of each person who participated in some part of Harvard Project Physics. Unhappily it is not feasible, since most staff members worked on a variety of materials and had multiple responsibilities. Furthermore, every text chapter, experiment, piece of apparatus, film or other item in the experimental program benefitted from the contributions of a great many people. On the preceding pages is a partial list of contributors to Harvard Project Physics. There were, in fact, many other contributors too numerous to mention. These include school administrators in participating schools, directors and staff members of training institutes for teachers, teachers who tried the course after the evaluation year, and most of all the thousands of students who not only agreed to take the experimental version of the course, but who were also willing to appraise it critically and contribute their opinions and suggestions.

The Project Physics Course Today. Using the last of the experimental versions of the course developed by Harvard Project Physics in 1964–68 as a starting point, and taking into account the evaluation results from the tryouts, the three original collaborators set out to develop the version suitable for large-scale publication. We take particular pleasure in acknowledging the assistance of Dr. Andrew Ahlgren of Harvard University. Dr. Ahlgren was invaluable because of his skill as a physics teacher, his editorial talent, his versatility and energy, and above all, his commitment to the goals of Harvard Project Physics.

We would also especially like to thank Miss Joan Laws whose administrative skills, dependability, and thoughtfulness contributed so much to our work. The publisher, Holt, Rinehart and Winston, Inc. of New York, provided the coordination, editorial support, and general backing necessary to the large undertaking of preparing the final version of all components of the Project Physics Course, including texts, laboratory apparatus, films, etc. Damon, a company located in Needham, Massachusetts, worked closely with us to improve the engineering design of the laboratory apparatus and to see that it was properly integrated into the program.

In the years ahead, the learning materials of the Project Physics Course will be revised as often as is necessary to remove remaining ambiguities, clarify instructions, and to continue to make the materials more interesting and relevant to students. We therefore urge all students and teachers who use this course to send to us (in care of Holt, Rinehart and Winston, Inc., 383 Madison Avenue, New York, New York 10017) any criticism or suggestions they may have.

F. James Rutherford
Gerald Holton
Fletcher G. Watson

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UNIT 5

Models of the Atom

CHAPTERS

- 17 The Chemical Basis of the Atomic Theory
- 18 Electrons and Quanta
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PROLOGUE In the earlier units of this course we studied the motion of bodies: bodies of ordinary size, such as we deal with in everyday life, and very large bodies, such as planets. We have seen how the laws of motion and gravitation were developed over many centuries and how they are used. We have learned about conservation laws, about waves, about light, and about electric and magnetic fields. All that we have learned so far can be used to study a problem which has intrigued people for many centuries: the problem of the nature of matter. The phrase, "the nature of matter," may seem simple to us now, but its meaning has been changing and growing over the centuries. The kind of questions and the methods used to find answers to these questions are continually changing. For example, during the nineteenth century the study of the nature of matter consisted mainly of chemistry: in the twentieth century the study of matter has also moved into atomic and nuclear physics.

Since 1800 progress has been so rapid that it is easy to forget that people have theorized about matter for more than 2,500 years. In fact some of the questions for which answers have been found only during the last hundred years began to be asked more than two thousand years ago. Some of the ideas we consider new and exciting, such as the atomic constitution of matter, were debated in Greece in the fifth and fourth centuries B.C. In this prologue we shall therefore review briefly the development of ideas concerning the nature of matter up to about 1800. This review will set the stage for the four chapters of Unit 5, which will be devoted, in greater detail, to the progress made since 1800 on understanding the constitution of matter. It will be shown in these chapters that matter is made up of discrete particles that we call atoms, and that the atoms themselves have structure.

The photographs on these two pages illustrate some of the variety of forms of matter: large and small, stable and shifting.



microscopic crystals



condensed water vapor

Opposite: Monolith—The Face of Half Dome (Photo by Ansel Adams)

Greek Ideas of Order

The Greek mind loved clarity and order, expressed in a way that still touches us deeply. In philosophy, literature, art and architecture it sought to interpret things in terms of humane and lasting qualities. It tried to discover the forms and patterns thought to be essential to an understanding of things. The Greeks delighted in showing these forms and patterns when they found them. Their art and architecture express beauty and intelligibility by means of balance of form and simple dignity.

These aspects of Greek thought are beautifully expressed in the shrine of Delphi. The theater, which could seat 5,000 spectators, impresses us because of the size and depth of the tiered seating structure. But even more striking is the natural and orderly way in which the theater is shaped into the landscape so that the entire landscape takes on the aspect of a giant theater. The Treasury building at Delphi has an orderly system of proportions, with form and function integrated into a logical, pleasing whole. The statue of the charioteer found at Delphi, with its balance and firmness, represents a genuine ideal of male beauty at that time. After more than 2,000 years we are still struck by the elegance of Greek expression.



The Roman poet Lucretius based his ideas of physics on the tradition of atomism dating back to the Greek philosophers Democritus and Leucippus. The following passages are from his poem *De Rerum Natura* (*On the Nature of Things*), an eloquent statement of atomism:

... If you think

Atoms can stop their course, refrain from movement,
And by cessation cause new kinds of motion,
You are far astray indeed. Since there is void
Through which they move, all fundamental motes
Must be impelled, either by their own weight
Or by some force outside them. When they strike
Each other, they bounce off; no wonder, either,
Since they are absolute solid, all compact,
With nothing back of them to block their path.

... no atom ever rests

Coming through void, but always drives, is driven
In various ways, and their collisions cause,
As the case may be, greater or less rebound.
When they are held in thickest combination,
At closer intervals, with the space between
More hindered by their interlock of figure,
These give us rock, or adamant, or iron,
Things of that nature. (Not very many kinds
Go wandering little and lonely through the void.)
There are some whose alternate meetings, partings, are
At greater intervals; from these we are given
Thin air, the shining sunlight . . .

* * *

... It's no wonder

That while the atoms are in constant motion,
Their total seems to be at total rest,
Save here and there some individual stir.
Their nature lies beyond our range of sense,
Far, far beyond. Since you can't get to see
The things themselves, they're bound to hide their moves,
Especially since things we can see, often
Conceal their movements, too, when at a distance.
Take grazing sheep on a hill, you know they move,
The woolly creatures, to crop the lovely grass
Wherever it may call each one, with dew
Still sparkling it with jewels, and the lambs,
Fed full, play little games, flash in the sunlight,
Yet all this, far away, is just a blue,
A whiteness resting on a hill of green.
Or when great armies sweep across great plains
In mimic warfare, and their shining goes
Up to the sky, and all the world around
Is brilliant with their bronze, and trampled earth
Trembles under the cadence of their tread,
White mountains echo the uproar to the stars,
The horsemen gallop and shake the very ground,
And yet high in the hills there is a place
From which the watcher sees a host at rest,
And only a brightness resting on the plain.
[translated from the Latin by Rolfe Humphries]

Early science had to develop out of the ideas available before science started—ideas that came from experience with snow, wind, rain, mist and clouds; with heat and cold; with salt and fresh water; wine, milk, blood, and honey; ripe and unripe fruit; fertile and infertile seeds. The most obvious and most puzzling facts were that plants, animals, and men were born, that they grew and matured, and that they aged and died. Men noticed that the world about them was continually changing and yet, on the whole, it seemed to remain much the same. The unknown causes of these changes and of the apparent continuity of nature were assigned to the actions of gods and demons who were thought to control nature. Myths concerning the creation of the world and the changes of the seasons were among the earliest creative productions of primitive peoples everywhere, and helped them to come to terms with events man could see happening but could not rationally understand.

Over a long period of time men developed some control over nature and materials: they learned how to keep warm and dry, to smelt ores, to make weapons and tools, to produce gold ornaments, glass, perfumes, and medicines. Eventually, in Greece, by the year 600 B.C., philosophers—literally “lovers of wisdom”—had started to look for rational explanations of natural events, that is, explanations that did not depend on the actions or the whims of gods or demons. They sought to discover the enduring, unchanging things out of which the world is made, and how these enduring things can give rise to the changes that we perceive, as well as the great variety of material things that exists. This was the beginning of man’s attempts to understand the material world rationally, and it led to a theory of the nature of matter.

The earliest Greek philosophers thought that all the different things in the world were made out of a single basic substance. Some thought that water was the fundamental substance and that all other substances were derived from it. Others thought that air was the basic substance; still others favored fire. But neither water, nor air, nor fire was satisfactory; no one substance seemed to have enough different properties to give rise to the enormous variety of substances in the world. According to another view, introduced by Empedocles around 450 B.C., there are four basic types of matter—earth, air, fire, and water—and all material things are made out of them. These four basic materials can mingle and separate and reunite in different proportions, and so produce the variety of familiar objects around us as well as the changes in such objects. But the basic four materials, called *elements*, were supposed to persist through all these changes. This theory was the first appearance in our scientific tradition of a *model of matter*, according to which all material things are just different arrangements of a few external elements.

The first atomic theory of matter was introduced by the Greek philosopher Leucippus, born about 500 B.C., and his pupil Democritus, who lived from about 460 B.C. to 370 B.C. Only scattered fragments of the writings of these philosophers remain, but their ideas were discussed in considerable detail by the Greek philosophers Aristotle (389–321 B.C.) and Epicurus (341–270 B.C.), and by the Latin poet



This gold earring, made in Greece about 600 B.C., shows the great skill with which ancient artisans worked metals. [Museum of Fine Arts, Boston]

Lucretius (100–55 B.C.). It is to these men that we owe most of our knowledge of ancient atomism.

The theory of the atomists was based on a number of assumptions:

- (1) matter is eternal—no material thing can come from nothing, nor can any material thing pass into nothing;
- (2) material things consist of very small indivisible particles—the word “atom” meant “uncuttable” in Greek and, in discussing the ideas of the early atomists, we could use the word “indivisibles” instead of the word “atoms”;
- (3) atoms differ chiefly in their sizes and shapes;
- (4) the atoms exist in otherwise empty space (the void) which separates them, and because of this space they are capable of movement from one place to another;
- (5) the atoms are in ceaseless motion, although the nature and cause of the motion are not clear;
- (6) in the course of their motions atoms come together and form combinations which are the material substances we know; when the atoms forming these combinations separate, the substances decay or break up. Thus, the combinations and separations of atoms give rise to the changes which take place in the world;
- (7) the combinations and separations take place in accord with natural laws which are not yet clear, but do not require the action of gods or demons or other supernatural powers.

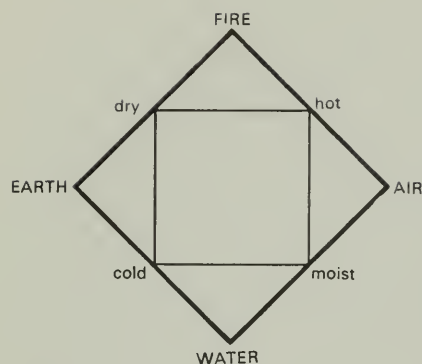
With the above assumptions, the ancient atomists were able to work out a consistent story of change, of what they sometimes called “coming-to-be” and “passing away.” They could not demonstrate experimentally that their theory was correct, and they had to be satisfied with an explanation derived from assumptions that seemed reasonable to them. The theory was a “likely story.” It was not useful for the prediction of new phenomena; but that became an important value for a theory only later. To these atomists, it was more significant that the theory also helped to allay the unreasonable fear of capricious gods.

The atomic theory was criticized severely by Aristotle, who argued logically—from his own assumptions—that no vacuum or void could exist and that the ideas of atoms with their continual motion must be rejected. (Aristotle was also probably sensitive to the fact that in his time atomism was identified with atheism.) For a long time Aristotle’s argument against the void was widely held to be convincing. One must here recall that not until the seventeenth century did Torricelli’s experiments (described in Chapter 11) show that a vacuum could indeed exist. Furthermore, Aristotle argued that matter is continuous and infinitely divisible so that there can be no atoms.

Aristotle developed a theory of matter as part of his grand scheme of the universe, and this theory, with some modifications, was thought to be satisfactory by most philosophers of nature for nearly two thousand years. His theory of matter was based on the four basic elements, Earth, Air, Fire, and Water, and four “qualities,” Cold, Hot, Moist, and Dry. Each element was characterized by two qualities (the

According to Aristotle in his *Metaphysics*, “There is no consensus concerning the number or nature of these fundamental substances. Thales, the first to think about such matters, held that the elementary substance is clear liquid. . . . He may have gotten this idea from the observation that only moist matter can be wholly integrated into an object—so that all growth depends on moisture. . . .

“Anaximenes and Diogenes held that colorless gas is more elementary than clear liquid, and that indeed, it is the most elementary of all simple substances. On the other hand Hippasus of Metapontum and Heraclitus of Ephesus said that the most elementary substance is heat. Empedocles spoke of four elementary substances, adding dry dust to the three already mentioned Anaxagoras of Clazomenae says that there are an infinite number of elementary constituents of matter. . . .” [From a translation by D. E. Gershenson and D. A. Greenberg]



nearer two to each side, as shown in the diagram at the left). Thus the element

Earth is Dry and Cold,
 Water is Cold and Moist,
 Air is Moist and Hot,
 Fire is Hot and Dry.

According to Aristotle, it is always the first of the two qualities which predominates. In his version the elements are not unchangeable; any one of them may be transformed into any other because of one or both of its qualities changing into opposites. The transformation takes place most easily between two elements having one quality in common; thus Earth is transformed into Water when dryness changes into moistness. Earth can be transformed into Air only if both of the qualities of earth (dry and cold) are changed into their opposites (moist and hot).

As we have already mentioned in the *Text* Chapter 2, Aristotle was able to explain many natural phenomena by means of his ideas. Like the atomic theory, Aristotle's theory of coming-to-be and passing-away was consistent, and constituted a model of the nature of matter. It had certain advantages over the atomic theory: it was based on elements and qualities that were familiar to people; it did not involve atoms, which couldn't be seen or otherwise perceived, or a void, which was most difficult to imagine. In addition, Aristotle's theory provided some basis for further experimentation: it supplied what seemed like a rational basis for the tantalizing possibility of changing any material into any other.

Although the atomistic view was not altogether abandoned, it found few supporters during the period 300 A.D. to about 1600 A.D. The atoms of Leucippus and Democritus moved through empty space, devoid of spirit, and with no definite plan or purpose. Such an idea remained contrary to the beliefs of the major religions. Just as the Athenians did in the time of Plato and Aristotle, the later Christian, Hebrew, and Moslem theologians considered atomists to be atheistic and "materialistic" because they claimed that everything in the universe can be explained in terms of matter and motion.

About 300 or 400 years after Aristotle, a kind of research called *alchemy* appeared in the Near and Far East. Alchemy in the Near East was a combination of Aristotle's ideas about matter with methods of treating ores and metals. One of the aims of the alchemists was to change, or "transmute" ordinary metals into precious metals. Although they failed to do this, the alchemists found and studied many of the properties of substances that are now classified as chemical properties. They invented some pieces of chemical apparatus, such as reaction vessels and distillation flasks, that (in modern form) are still common in chemical laboratories. They studied such processes as calcination, distillation, fermentation, and sublimation. In this sense alchemy may be regarded as the chemistry of the Middle Ages. But alchemy left unsolved the fundamental questions. At the opening of the eighteenth century the most important of these questions were: (1) what is a chemical element; (2) what is the nature of chemical composition and chemical change, especially burning; and (3) what is the chemical



Laboratory of a 16th-century alchemist.

nature of the so-called elements, Earth, Air, Fire and Water. Until these questions were answered, it was impossible to make real progress in finding out the structure of matter. One result was that the “scientific revolution” of the seventeenth century, which clarified the problems of astronomy and mechanics, did not include chemistry.

During the seventeenth century, however, some forward steps were made which supplied a basis for future progress on the problem of matter. The Copernican and Newtonian revolutions undermined the authority of Aristotle to such an extent that his ideas about matter were also more easily questioned. Atomic concepts were revived, and offered a way of looking at things that was very different from Aristotle’s ideas. As a result, theories involving atoms (or “particles” or “corpuscles”) were again considered seriously. Boyle’s models were based on the idea of “gas particles.” Newton also discussed the behavior of a gas (and even of light) by supposing it to consist of particles. In addition, there was now a successful science of mechanics, through which one might hope to describe how the atoms interacted with each other. Thus the stage was set for a general revival of atomic theory.

In the eighteenth century, chemistry became more quantitative; weighing in particular was done more frequently and more carefully. New substances were isolated and their properties examined. The attitude that grew up in the latter half of the century was exemplified by that of Henry Cavendish (1731–1810), who, according to a biographer, regarded the universe as consisting

... solely of a multitude of objects which could be weighed, numbered, and measured; and the vocation to which he considered himself called was to weigh, number, and measure as many of those objects as his allotted threescore years and ten would permit. . . . He weighed the Earth; he analysed the Air; he discovered the compound nature of Water; he noted with numerical precision the obscure actions of the ancient element Fire.

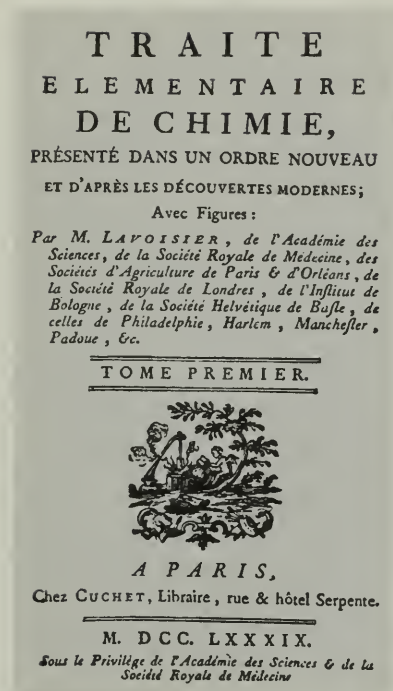
Eighteenth-century chemistry reached its peak in the work of Antoine Lavoisier (1743–1794), who worked out the modern views of combustion, established the law of conservation of mass, explained the elementary nature of hydrogen and oxygen, and the composition of water, and above all emphasized the quantitative aspects of chemistry. His famous book, *Traité Élémentaire de Chimie* (or *Elements of Chemistry*), published in 1789, established chemistry as a modern science. In it, he analyzed the idea of an element in a way which is very close to our modern views:

... if, by the term *elements* we mean to express those simple and indivisible atoms of which matter is composed, it is extremely probable that we know nothing at all about them; but if we apply the term *elements*, or *principles of bodies*, to express our idea of the last point which analysis is capable of reaching, we must admit as elements all the substances into which we are capable, by any means, to reduce bodies by decomposition. Not that we are entitled to affirm that

One of those who contributed greatly to the revival of atomism was Pierre Gassendi (1592–1655), a French priest and philosopher. He avoided the criticism of atomism as atheistic by saying that God also created the atoms and bestowed motion upon them. Gassendi accepted the physical explanations of the atomists, but rejected their disbelief in the immortality of the soul and in Divine Providence. He was thus able to provide a philosophical justification of atomism which met some of the serious religious objections.

It was Cavendish, remember, who designed the sensitive torsional balance that made it possible to find a value for the gravitational constant G . (Text Sec. 8.8.)

Lavoisier’s work on the conservation of mass was described in Text Chapter 9.



Title page of Lavoisier's *Traité Élémentaire de Chimie* (1789)

these substances we consider as simple may not be compounded of two, or even of a greater number of principles; but since these principles cannot be separated, or rather since we have not hitherto discovered the means of separating them, they act with regard to us as simple substances, and we ought never to suppose them compounded until experiment and observation have proved them to be so.

During the latter half of the eighteenth century and the early years of the nineteenth century great progress was made in chemistry because of the increasing use of quantitative methods. Chemists found out more and more about the composition of substances. They separated many elements and showed that nearly all substances are *compounds*—combinations of a fairly small number of chemical elements. They learned a great deal about how elements combine to form compounds and how compounds can be broken down into the elements of which they are composed. This information made it possible for chemists to establish many empirical laws of chemical combination. Then chemists sought an explanation for these laws.

During the first ten years of the nineteenth century, the English chemist John Dalton introduced a modified form of the old Greek atomic theory to account for the laws of chemical combination. It is here that the modern story of the atom begins. Dalton's atomic theory was an improvement over that of the Greeks because it opened the way for the quantitative study of the atom in the nineteenth century. Today the existence of the atom is no longer a topic of speculation. There are many kinds of experimental evidence, not only for the existence of atoms but also for their inner structure. In this unit we shall trace the discoveries and ideas that provided this evidence.

The first convincing modern idea of the atom came from chemistry. We shall, therefore, start with chemistry in the early years of the nineteenth century; this is the subject of Chapter 17. Then we shall see that chemistry raised certain questions about atoms which could only be answered by physics. Physical evidence, accumulated in the nineteenth century and the early years of the twentieth century, made it possible to propose models for the structure of atoms. This evidence will be discussed in Chapters 18 and 19. Some of the latest ideas about atomic theory will then be discussed in Chapter 20.



Chemical laboratory of the 18th century

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Dalton's symbols for "elements" (1808)

CHAPTER SEVENTEEN

The Chemical Basis of Atomic Theory

17.1 Dalton's atomic theory and the laws of chemical combination

The atomic theory of John Dalton appeared in his treatise, *A New System of Chemical Philosophy*, published in two parts, in 1808 and 1810. The main postulates of his theory were:

- (1) Matter consists of indivisible atoms.

SG 17.1

... matter, though divisible in an *extreme degree*, is nevertheless not *infinitely* divisible. That is, there must be some point beyond which we cannot go in the division of matter. The existence of these ultimate particles of matter can scarcely be doubted, though they are probably much too small ever to be exhibited by microscopic improvements. I have chosen the word *atom* to signify these ultimate particles. . . .

- (2) Each element consists of a characteristic kind of identical atoms. There are consequently as many different kinds of atoms as there are elements. The atoms of an element “are perfectly alike in weight and figure, etc.”

- (3) Atoms are unchangeable.

- (4) When different elements combine to form a compound, the smallest portion of the compound consists of a grouping of a definite number of atoms of each element.

- (5) In chemical reactions, atoms are neither created nor destroyed, but only rearranged.

Dalton's theory really grew out of his interest in meteorology and his research on the composition of the atmosphere. He tried to explain many of the physical properties of gases in terms of atoms (for example, the fact that gases readily mix, and the fact that the pressures of two gases add simply when both are combined in a fixed enclosure). He thought of the atoms of different elements as being different in size and in mass. In keeping with the quantitative spirit of the time, he tried to determine the numerical values for their relative masses. This was a crucial step forward. But before considering how to determine the relative masses of atoms of the different elements, let us see how Dalton's postulates make it possible to account for the experimentally known laws of chemical combination.

Meteorology is a science that deals with the atmosphere and its phenomena—weather forecasting is one branch of meteorology

Dalton's atomic theory accounts in a simple and direct way for the law of conservation of mass. According to Dalton's theory (postulates 4 and 5), chemical changes are only the rearrangements of unions of atoms. Since atoms are unchangeable (according to postulate 3) rearranging them cannot change their masses. Hence, the total mass of all the atoms before the reaction must equal the total mass of all the atoms after the reaction.

Another well known empirical law which could be explained easily with Dalton's theory is the *law of definite proportions*. This law states that any particular chemical compound always contains the same elements, and they are united in the same proportions of weight. For example, the ratio of the masses of oxygen and hydrogen which combine to form water is always 7.94 to 1:

$$\frac{\text{mass of oxygen}}{\text{mass of hydrogen}} = \frac{7.94}{1}$$

If there is more of one element present than is needed for full combination in a chemical reaction, say 10 grams of oxygen and one gram of hydrogen, only 7.94 grams of oxygen will combine with the hydrogen. The rest of the oxygen, 2.06 grams, remains uncombined.

The fact that elements combine in fixed proportions implies that each chemical compound will also decompose into definite proportions of elements. For example, the decomposition of sodium chloride (common salt) always gives the results: 39 percent sodium and 61 percent chlorine by weight.

Now let us see how Dalton's model can be applied to a chemical reaction, say, to the formation of water from oxygen and hydrogen. According to Dalton's second postulate, all the atoms of oxygen have the same mass; and all the atoms of hydrogen have the same mass, which is different from the mass of the oxygen atoms. To express the total mass of oxygen entering into the reaction, we multiply the mass of a single oxygen atom by the number of oxygen atoms:

SG 17.2, 17.3

$$\text{mass of oxygen} = \left(\frac{\text{mass of}}{\text{oxygen atom}} \right) \times \left(\frac{\text{number of}}{\text{oxygen atoms}} \right)$$

Similarly, for the total mass of hydrogen entering into the reaction:

$$\text{mass of hydrogen} = \left(\frac{\text{mass of}}{\text{hydrogen atom}} \right) \times \left(\frac{\text{number of}}{\text{hydrogen atoms}} \right)$$

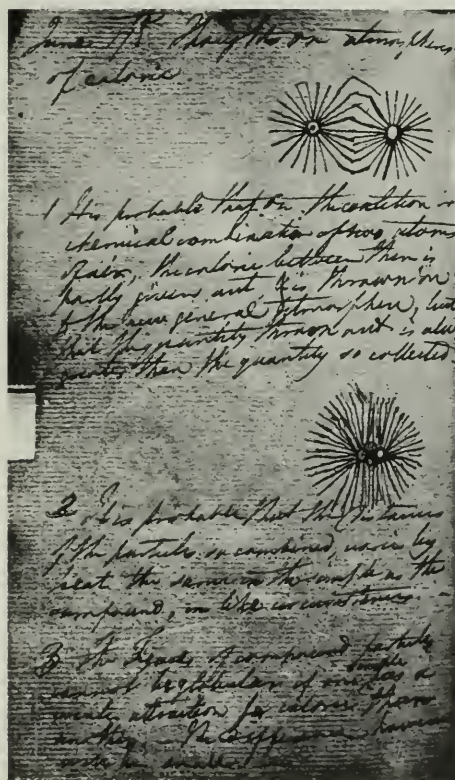
We can find the ratio of the mass of oxygen to the mass of hydrogen by dividing the first equation by the second equation as shown at the top of the next page:

Recall that empirical laws (such as these, or Kepler's laws of planetary motion) are just summaries of experimentally observed facts. They cry out for some theoretical base from which they can be shown to follow as necessary consequences. Physical science looks for these deeper necessities that describe nature, and is not satisfied with mere summaries of observation, useful though these may be initially.

$$\frac{\text{mass of oxygen}}{\text{mass of hydrogen}} = \frac{\text{mass of oxygen atom}}{\text{mass of hydrogen atom}} \times \frac{\text{number of oxygen atoms}}{\text{number of hydrogen atoms}}$$

SG 17.4

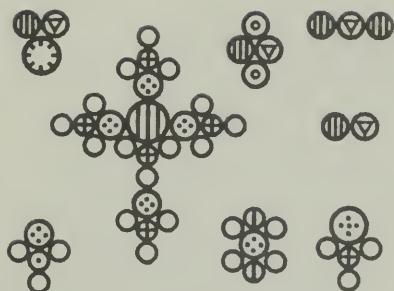
If the masses of the atoms do not change (postulate 3), the first ratio on the right side of the equation has a certain unchangeable value. According to postulate 4, if the smallest portion of the compound water consists of a definite number of atoms of each element (postulate 4), the second ratio on the right side of the equation has a certain unchangeable value also. The product of the two ratios on the right side will always have the same value. This equation, based on an atomic theory, thus tells us that the ratio of the masses of oxygen and hydrogen that combine to form water will always have the same definite value. But this is just what the experimental law of definite proportions says. Dalton's theory accounts for this law of chemical combination—and this success tends to confirm Dalton's conception. Dalton's theory was also consistent with another empirical law of chemical combination, the *law of multiple proportion*. For some combinations of elements there are a set of possible values for their proportions in forming a



A page from Dalton's notebook, showing his representation of two adjacent atoms (top) and of a molecule or "compound atom" (bottom)

John Dalton (1766–1844). His first love was meteorology, and he kept careful daily weather records for 46 years—a total of 200,000 observations. He was the first to describe color blindness in a publication and was color-blind himself, not exactly an advantage for a chemist who had to see color changes in chemicals. (His color blindness may help to explain why Dalton is said to have been a rather clumsy experimenter.) However, his accomplishments rest not on successful experiments, but on his ingenious interpretation of the known results of others. Dalton's notion that all elements were composed of extremely tiny, indivisible and indestructible atoms, and that all substances are composed of combinations of these atoms was accepted soon by most chemists with surprisingly little opposition. There were many attempts to honor him, but being a Quaker he shunned any form of glory. When he received a doctor's degree from Oxford, his colleagues wanted to present him to King William IV. He had always resisted such a presentation because he would not wear court dress. However, his Oxford robes satisfied the protocol.





Dalton's visualization of the composition of various compounds.

set of compounds. Dalton showed that these cases could all be accounted for by different combinations of whole numbers of atoms.

There are other laws of chemical combination which are explained by Dalton's theory. Because the argument would be lengthy and relatively little that is new would be added, we shall not elaborate on them here.

Dalton's interpretation of the experimental facts of chemical combination made possible several important conclusions: (1) that the difference between one chemical element and another would have to be described in terms of the differences between the atoms of which these elements were made up; (2) that there were, therefore, as many different types of atoms as there were chemical elements; (3) that chemical combination was the union of atoms of different elements into molecules of compounds. Dalton's theory also implied that the analysis of a large number of chemical compounds could make it possible to assign relative mass values to the atoms of different elements. This possibility will be discussed in the next section.

Q1 What did Dalton *assume* about the atoms of an element?

Q2 What two *experimental* laws did Dalton's theory explain?
What follows from these successes?

The first good estimates of molecular size came from the kinetic theory of gases and indicated that atoms (or molecules) had diameters of the order of 10^{-10} meter. Atoms are thus much too small for ordinary mass measurements to be made on single atoms.

17.2 The atomic masses of the elements

One of the most important concepts to come from Dalton's work is that of atomic mass and the possibility of determining numerical values for the masses of the atoms of different elements. Dalton had no idea of the actual absolute mass of individual atoms. Reasonably good estimates of the size of atoms did not appear until about 50 years after Dalton published his theory. Nevertheless, as Dalton was able to show, *relative* values of atomic masses can be found by using the law of definite proportions and experimental data on chemical reactions.

To see how this could be done we return to the case of water, for which, the ratio of the mass of oxygen to the mass of hydrogen is found by experiment to be 7.94:1. If one knew how many atoms of oxygen and hydrogen are contained in a molecule of water one could calculate the ratio of the mass of the oxygen atom to the mass of the hydrogen atom. But Dalton didn't know the numbers of oxygen and hydrogen atoms in a molecule of water so he made an assumption. As is done often, Dalton made the *simplest* possible assumption: that a molecule of water consists of *one* atom of oxygen combined with *one* atom of hydrogen. By this reasoning Dalton concluded that the oxygen atom is 7.94 times more massive than the hydrogen atom. Actually, the simplest assumption proved in this case to be incorrect: *two* atoms of hydrogen combine with one atom of oxygen to make a molecule of water. The oxygen atom has 7.94 times the mass of the two hydrogen atoms, and therefore has 15.88 times the mass of a single hydrogen atom.

More generally, Dalton assumed that when only one compound

of any two elements is known to exist, molecules of the compound always consist of one atom of each. With this assumption Dalton could find values for the relative masses of different atoms—but later work showed that Dalton's assumption of one-to-one ratios was often as incorrect as it was for water. By studying the composition of water as well as many other chemical compounds, Dalton found that the hydrogen atom appeared to have a smaller mass than the atoms of any other element. Therefore, he proposed to express the masses of atoms of all other elements relative to the mass of the hydrogen atom. Dalton defined the *atomic mass* of an element as the mass of an atom of that element compared to the mass of a hydrogen atom. For example, the masses of chlorine and hydrogen gas that react to form hydrogen chloride (the only hydrogen and chlorine compound) are in the ratio of about $35\frac{1}{2}$ to 1; therefore the chlorine atom would be supposed to have an atomic mass of $35\frac{1}{2}$ atomic mass units. This definition could be used by chemists in the nineteenth century even before the actual values of the masses of individual atoms (say in kilograms) could be measured directly.

During the nineteenth century chemists extended and improved Dalton's ideas. They studied many chemical reactions quantitatively, and developed highly accurate methods for determining relative atomic and molecular masses. Because oxygen combined readily with many other elements chemists decided to use oxygen rather than hydrogen as the standard for atomic masses. Oxygen was assigned an atomic mass of 16 so that hydrogen would have an atomic mass close to one. The atomic masses of other elements could be obtained by applying the laws of chemical combination to the compounds of the elements with oxygen. Throughout the nineteenth century more and more elements were identified and their atomic masses determined. For example, the table on the next page lists 63 elements found by 1872, together with the modern values for the atomic masses. This table contains much valuable information, which we shall consider at greater length in Sec. 17.4. (The special marks on the table—circles and rectangles—will be useful then.)

Q3 Was the simplest chemical formula for the composition of a molecule necessarily the correct one?

Q4 Why did Dalton choose hydrogen as the unit of atomic mass?

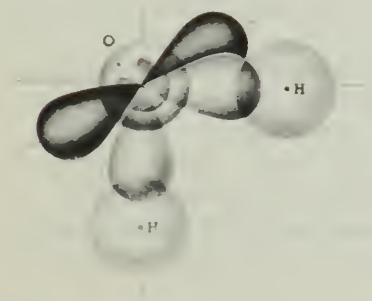
SG 17.7

SG 17.8

The system of atomic masses used in modern physical science is based on this principle, although it differs in details (and the standard for comparison by international agreement is now carbon instead of hydrogen or oxygen.)

The progress made in identifying elements in the 19th century may be seen in the following table.

Year	Total number of elements identified
1720	14
1740	15
1760	17
1780	21
1800	31
1820	49
1840	56
1860	60
1880	69
1900	83



Some of the current representations of a water molecule.

Elements known by 1872, in order of increasing relative atomic mass.

Elements known by 1872					
Name	Symbol	Atomic Mass*	Name	Symbol	Atomic Mass*
hydrogen	H	1.0	cadmium	Cd	112.4
<input type="checkbox"/> lithium	Li	6.9	indium	In	114.8(113)
beryllium	Be	9.0	tin	Sn	118.7
boron	B	10.8	antimony	Sb	121.7
carbon	C	12.0	tellurium	Te	127.6(125)
nitrogen	N	14.0	<input type="radio"/> iodine	I	126.9
oxygen	O	16.0	<input type="checkbox"/> cesium	Cs	132.9
<input type="radio"/> fluorine	F	19.0	barium	Ba	137.3
<input type="checkbox"/> sodium	Na	23.0	didymium(**)	Di	— (138)
magnesium	Mg	24.3	cerium	Ce	140.1
aluminum	Al	27.0	erbium	Er	167.3(178)
silicon	Si	28.1	lanthanum	La	138.9(180)
phosphorus	P	31.0	tantalum	Ta	180.9(182)
sulfur	S	32.1	tungsten	W	183.9
<input type="radio"/> chlorine	Cl	35.5	osmium	Os	190.2(195)
<input type="checkbox"/> potassium	K	39.1	iridium	Ir	192.2(197)
calcium	Ca	40.1	platinum	Pt	195.1(198)
titanium	Ti	47.9	gold	Au	197.0(199)
vanadium	V	50.9	mercury	Hg	200.6
chromium	Cr	52.0	thallium	Tl	204.4
manganese	Mn	54.9	lead	Pb	207.2
iron	Fe	55.8	bismuth	Bi	209.0
cobalt	Co	58.9	thorium	Th	232.0
nickel	Ni	58.7	uranium	U	238.0(240)
copper	Cu	63.5			
zinc	Zn	65.4			
arsenic	As	74.9	<input type="checkbox"/> alkaline metals		
selenium	Se	79.0	<input type="radio"/> halogens		
<input type="radio"/> bromine	Br	79.9			
<input type="checkbox"/> rubidium	Rb	85.5			
strontium	Sr	87.6			
yttrium	Yt	88.9			
zirconium	Zr	91.2			
niobium	Nb	92.9			
molybdenum	Mo	95.9			
ruthenium	Ru	101.1(104)			
rhodium	Rh	102.9(104)			
palladium	Pd	106.4			
silver	Ag	107.9			

*Atomic masses given are modern values. Where these differ greatly from those accepted in 1872, the old values are given in parentheses.

**Didymium (Di) was later shown to be a mixture of two different elements, namely praseodymium (Pr; atomic mass 140.9) and neodymium (Nd; atomic mass 144.2).

17.3 Other properties of the elements: combining capacity

As a result of studies of chemical compounds, chemists were able to design chemical *formulas* that indicate by a kind of symbolic shorthand the number of atoms in each molecule of a compound. For example, water has the familiar formula H_2O , which indicates that a molecule of water contains two atoms of hydrogen (H) and one atom of oxygen (O). (Dalton thought it was HO .) Hydrogen chloride (hydrochloric acid when dissolved in water) had the formula HCl , signifying that one atom of hydrogen combines with one atom of chlorine (Cl). Common salt may be represented by the formula NaCl ; this indicates that one atom of sodium (Na) combines with one atom of chlorine to form one molecule of sodium chloride—common table salt. Another salt, calcium chloride (often used to melt ice on roads), has the formula CaCl_2 ; one atom of calcium (Ca) combined with two atoms of chlorine to form this compound. Carbon tetrachloride, a common compound of chlorine used for dry

The standard international chemical symbols are derived from languages other than English. The Latin name for sodium is *natrium*, hence the symbol is Na.

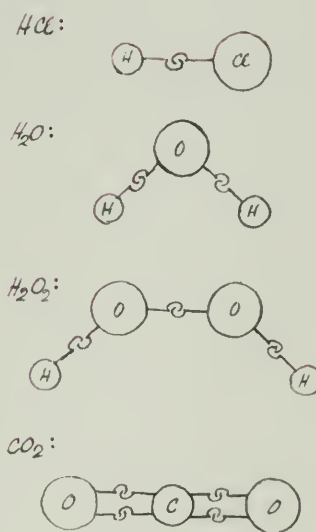
cleaning, has the formula CCl_4 where C stands for a carbon atom that combines with four chlorine atoms. Another common substance, ammonia, has the formula NH_3 ; in this case one atom of nitrogen (N) combines with three atoms of hydrogen.

There are especially significant examples of combining capacity among the gaseous elements. For example, the gas hydrogen occurs in nature in the form of molecules, each of which contains two hydrogen atoms. The molecule of hydrogen consists of two atoms and has the formula H_2 . Similarly, chlorine has the molecular formula Cl_2 . Chemical analysis always gives these results. It would be inconsistent with experiment to assign the formula H_3 or H_4 to a molecule of hydrogen, or Cl , Cl_3 , or Cl_4 to a molecule of chlorine. Moreover, each element shows great consistency in its combining proportions with other elements. For example, calcium and oxygen seem to have twice the combining capacity of hydrogen and chlorine—one atom of hydrogen is enough for one atom of chlorine, but two hydrogens are needed to combine with oxygen and two chlorines are required to combine with calcium.

The above examples indicate that different elements have different capacities for chemical combination. It appeared that each species of atom is characterized by some definite combining capacity (which is sometimes called *valence*). At one time combining capacity was considered as though it might represent the number of “hooks” possessed by a given atom, and thus the number of links that an atom could form with others of the same or different species. If hydrogen and chlorine atoms each had just one hook (that is, a combining capacity of 1) we would readily understand how it is that molecules like H_2 , Cl_2 , and HCl are stable, while certain other species like H_3 , H_2Cl , HCl_2 , and Cl_3 don’t exist at all. And if the hydrogen atom is thus assigned a combining capacity of 1, the formula of water (H_2O) requires that the oxygen atom has two hooks or a combining capacity of 2. The formula NH_3 for ammonia leads us to assign a combining capacity of three to nitrogen; the formula CH_4 for methane leads us to assign a capacity of 4 to carbon; and so on. Proceeding in this fashion, we can assign a combining capacity number to each of the known elements. Sometimes complications arise as, for example, in the case of sulfur. In H_2S the sulfur atom seems to have a combining capacity of 2, but in such a compound as sulfur trioxide (SO_3), sulfur seems to have a combining capacity of 6. In this case and others, then, we may have to assign two (or even more) different possible capacities to an element. At the other extreme of possibilities are those elements like helium and neon which have not been found as parts of compounds—and to these elements we may appropriately assign a combining capacity of zero.

The atomic mass and combining capacities are numbers that can be assigned to an element; they are “numerical characterizations” of the atoms of the element. There are other numbers which represent properties of the atoms of the elements, but atomic mass and combining capacity were the two most important to nineteenth-

In the thirteenth century the theologian and philosopher Albert Magnus (Albert the Great) introduced the idea of *affinity* to denote an attractive force between substances that causes them to enter into chemical combination. It was not until 600 years later that it became possible to replace this qualitative notion by *quantitative* concepts. Combining capacity is one of these concepts.



Representations of molecules formed from “atoms with hooks.” Of course this conception is just a guide to the imagination. There are no such mechanical linkages among atoms.

SG 17.9

Since oxygen combines with a greater variety of elements, combining capacity of an element was commonly determined by its combination with oxygen. For example, an element X that is found to have an “oxide formula” XO would have a combining capacity equal to oxygen’s: 2.

century chemists. These numbers were used in attempts to find order and regularity among the elements—a problem which will be discussed in the next section.

Q5 At this point we have two numbers which are characteristic of the atoms of an element. What are they?

Q6 Assume the combining capacity of oxygen is 2. In each of the following molecules, give the combining capacity of the atoms other than oxygen: CO , CO_2 , N_2O_5 , Na_2O and MnO .

17.4 The search for order and regularity among the elements

By 1872 sixty-three elements were known; they are listed in the table on p. 16 with their atomic masses and chemical symbols. Sixty-three elements are many more than Aristotle's four: and chemists tried to make things simpler by looking for ways of organizing what they had learned about the elements. They tried to find relationships among the elements—a quest somewhat like Kepler's earlier search for rules that would relate the motions of the planets of the solar system.

In addition to relative atomic masses, many other properties of the elements and their compounds were determined. Among these properties were: melting point, boiling point, density, electrical conductivity, heat conductivity, heat capacity (the amount of heat needed to change the temperature of a sample of a substance by 1°C) hardness, and refractive index. The result was that by 1870 an enormous amount of information was available about a large number of elements and their compounds.

It was the English chemist J. A. R. Newlands who pointed out in 1865 that the elements could usefully be listed simply in the order of increasing atomic mass. When this was done, a curious fact became evident; similar chemical and physical properties appeared over and over again in the list. Newlands believed that there was in the whole list a periodic recurrence of elements with similar properties: "... the eighth element, starting from a given one, is a kind of repetition of the first, like the eighth note in an octave of music." Newlands' proposal was met with skepticism. One chemist even suggested that Newlands might look for a similar pattern in an alphabetical list of elements.

Yet, existent relationships did indeed appear. There seemed to be families of elements with similar properties. One such family consists of the so-called *alkali metals*—lithium, sodium, potassium, rubidium and cesium. We have identified these elements by a \square in the table on p. 16. All these metals are similar physically. They are soft and have low melting points. The densities of these metals are very low; in fact, lithium, sodium and potassium are less dense than water. The alkali metals are also similar chemically. They all have combining capacity 1. They all combine with the same other elements to form similar compounds. They form compounds readily with other elements, and so are said to be highly "reactive"; conse-

There were also many false trails. Thus in 1829 the German chemist Johann Wolfgang Dobereiner noticed that elements often formed groups of three members with similar chemical properties. He identified the "triads": chlorine, bromine and iodine; calcium, strontium and barium; sulfur, selenium and tellurium; iron, cobalt and manganese. In each "triad," the atomic mass of the middle member was approximately the arithmetical average of the masses of the other two elements. But all this turned out to be of little significance.

quently, they do not occur free in nature, but are always found in combination with other elements.

Another family of elements, called the *halogens*, includes fluorine, chlorine, bromine and iodine. The halogens may be found in the table on p. 16 identified by small circles.

Although these four halogen elements exhibit some marked dissimilarities (for example, at 25 °C the first two are gases, the third a liquid, the last a volatile solid), they also have much in common. They all combine violently with many metals to form white, crystalline salts (*halogen* means “salt-former”); those salts have similar formulas, such as NaF, NaCl, NaBr and NaI, or MgF₂, MgCl₂, MgBr₂ and MgI₂. From much similar evidence chemists noticed that all four members of the family seem to have the same valence with respect to any other particular element. All four elements form simple compounds with hydrogen (HF, HCl, HBr, HI) which dissolve in water and form acids. All four, under ordinary conditions, exist as diatomic molecules; that is, each molecule contains two atoms. But notice: each halogen precedes an alkali metal in the list, although the listing was ordered simply by increasing atomic mass. It is as if some new pattern is coming out of a jig-saw puzzle.

The elements which follow the alkali metals in the list also form a family, the one called the *alkaline earth family*; this family includes beryllium, magnesium, calcium, strontium and barium. Their melting points and densities are higher than those of the alkali metals. The alkaline earths all have a valence of two. They react easily with many elements, but not as easily as do the alkali metals.

Recognition of the existence of these families of elements encouraged chemists to look for a systematic way of arranging the elements so that the members of a family would group together. Many schemes were suggested; the most successful and far reaching was that of the Russian chemist D. I. Mendeleev.

Q7 What are those properties of elements which recur systematically with increasing atomic mass?

17.5 Mendeleev's periodic table of the elements

Mendeleev, examining the properties of the elements, reached the conclusion that the atomic mass was the fundamental “numerical characterization” of each element. He discovered that if the elements were arranged in a table in the order of their atomic masses—but in a special way, a bit like cards laid out in the game of solitaire—the different chemical families turned out to fall into the different vertical columns of the table. There was no evident physical reason why this should be so, but it was a hint toward some remarkable connection among all elements.

Li 7	Be 9.4	B 11	C 12	N 14	O 16	F 19
Na 23	Mg 24	Al 27.4	Si 28	P 31	S 32	Cl 35.3
K 39	Ca 40	Ti 50	V 51		...etc.

Modern chemists use the word “valence” less and less in the sense we use it here. They are more likely to discuss “combining number” or “oxidation number.” Even the idea of a definite valence number for an element has changed, since combining properties can be different under different conditions.

Although the properties of elements do recur periodically with increasing atomic weight, Newlands had not realized that the separation of similar elements in the list becomes greater for the heavier elements.

In this table, hydrogen was omitted because of its unique properties. Helium and the other elements of the family of “noble gases” had not yet been discovered.



Dmitri Ivanovich Mendeleev (men-deh-lay'-ef) (1834–1907) received his first science lessons from a political prisoner who had been previously banished to Siberia by the Czar. Unable to get into college in Moscow, he was accepted in St. Petersburg, where a friend of his father had some influence. In 1866 he became a professor of chemistry there: in 1869 he published his first table of the sixty-three then known elements arranged according to increasing atomic mass. His paper was translated into German at once and so became known to scientists everywhere. Mendeleev came to the United States, where he studied the oil fields of Pennsylvania in order to advise his country on the development of the Caucasian resources. His liberal political views caused him often to be in trouble with the oppressive regime of the Czars.

As in the table on the preceding page, Mendeleev set down seven elements, from lithium to fluorine, in order of increasing atomic masses, and then put the next seven, from sodium to chlorine, in the second row. The periodicity of chemical behavior is already evident before we go on to write the third row. In the first column on the left are the first two alkali metals. In the seventh column are the first two members of the family of halogens. Indeed, within *each* of the columns the elements are chemically similar, having, for example, the same characteristic combining capacity.

When Mendeleev added a third row of elements, potassium (K) came below elements Li and Na, which are members of the same family and have the same oxide formula, X_2O , and the same combining capacity 1. Next in the row is Ca, oxide formula XO as with Mg and Be above it. In the next space to the right, the element of next higher atomic mass should appear. Of the elements known at the time, the next heavier was titanium (Ti), and it was placed in this space, right below aluminum (Al) and boron (B) by various workers who had tried to develop such schemes. Mendeleev, however, recognized that titanium (Ti) has chemical properties similar to those of carbon (C) and silicon (Si). For example, a pigment, titanium white, TiO_2 , has a formula comparable to CO_2 and SiO_2 . Therefore he concluded that titanium should be put in the *fourth* column. Then, if all this is not just a game but has deeper meaning, Mendeleev thought, there should exist a hitherto unsuspected element with atomic mass between that of calcium (40) and titanium (50), and with an oxide X_2O_3 . Here was a definite prediction. Mendeleev found also other cases of this sort among the remaining elements when they were added to this table of elements with due regard to the family properties of elements in each column.

The table below is Mendeleev's periodic system, or "periodic table" of the elements, as proposed in 1872. He distributed the 63 elements then known (with 5 in doubt) in 12 horizontal rows or *series*, starting with hydrogen in a unique separated position at the top left, and ending with uranium at the bottom right. All elements

GROUP→		I	II	III	IV	V	VI	VII	VIII
Higher oxides and hydrides		R_2O	RO	R_2O_3	RO_2 H_4R	R_2O_5 H_3R	RO_3 H_2R	R_2O_7 HR	RO_4
SERIES	1	H(1)							
	2	Li(7)	Be(9.4)	B(11)	C(12)	N(14)	O(16)	F(19)	
	3	Na(23)	Mg(24)	Al(27.3)	Si(28)	P(31)	S(32)	Cl(35.5)	
	4	K(39)	Ca(40)	—(44)	Ti(48)	V(51)	Cr(52)	Mn(55)	Fe(56), Co(59), Ni(59), Cu(63)
	5	[Cu(63)]	Zn(65)	—(68)	—(72)	As(75)	Se(78)	Br(80)	
	6	Rb(85)	Sr(87)	?Yt(88)	Zr(90)	Nb(94)	Mo(96)	—(100)	Ru(104), Rh(104), Pd(106), Ag(108)
	7	[Ag(108)]	Cd(112)	In(113)	Sn(118)	Sb(122)	Te(125)	I(127)	
	8	Cs(133)	Ba(137)	?Di(138)	?Ce(140)				
	9								
	10			?Er(178)	?La(180)	Ta(182)	W(184)		Os(195), Ir(197), Pt(198), Au(199)
	11	[Au(199)]	Hg(200)	Tl(204)	Pb(207)	Bi(208)			
	12				Th(231)		U(240)		

Periodic classification of the elements; Mendeleev, 1872.

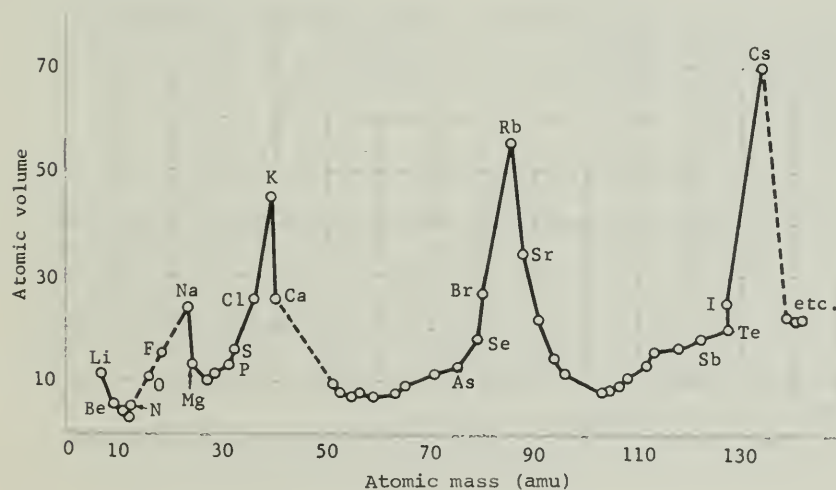
were listed in order of increasing atomic mass (Mendeleev's values given in parentheses), but were so placed that elements with similar chemical properties are in the same vertical column or *group*. Thus in Group VII are all the halogens; in Group VIII, only metals that can easily be drawn into wires; in Groups I and II, metals of low densities and melting points; and in I, the family of alkali metals.

The table at the bottom of the previous page shows many gaps. Also, not all horizontal rows (series) have equally many elements. Nonetheless, the table revealed an important generalization; according to Mendeleev,

For a true comprehension of the matter it is very important to see that all aspects of the distribution of the elements according to the order of their atomic weights express essentially one and the same fundamental dependence—*periodic properties*.

There is gradual change in physical and chemical properties within each vertical group, but there is a more striking periodic change of properties in the horizontal sequence.

This *periodic law* is the heart of the matter and a real novelty. Perhaps we can best illustrate it as Lothar Meyer did, by drawing a graph that shows the value of some measureable physical quantity as a function of atomic mass. Below is a plot of the relative *atomic volumes* of the elements, the space taken up by an atom in the liquid or solid state. Each circled point on this graph represents an element; a few of the points have been labeled with the identifying chemical symbols. Viewed as a whole, the graph demonstrates a striking periodicity: as the mass increases starting with Li, the atomic volume first drops, then increases to a sharp maximum, drops off again and increases to another sharp maximum, and so on. And at the successive peaks we find Li, Na, K, Rb, and Cs, the members of the family of alkali metals. On the left-hand side of each peak, there is one of the halogens.



The "atomic volume" is defined as the atomic mass divided by the density of the element in its liquid or solid state.

In 1864, the German chemist Lothar Meyer wrote a chemistry textbook. In this book, he considered how the properties of the chemical elements might depend on their atomic masses. He later found that if he plotted atomic volume against the atomic mass, the line drawn through the plotted points rose and fell in two long periods. This was exactly what Mendeleev had discovered in connection with valence. Mendeleev published his first result in 1869. Meyer, as he himself later admitted, lacked the courage to include provision for empty spaces that would amount to the prediction of the discovery of unknown elements. Nevertheless, Meyer should be given credit for the idea of the periodic table.

The atomic volumes of elements graphed against their atomic masses.

Mendeleev's periodic table of the elements not only provided a remarkable correlation of the elements and their properties, it also enabled him to predict that certain unknown elements should exist and what many of their properties should be. To estimate physical properties of a missing element, Mendeleev averaged the properties of its nearest neighbors in the table: those to right and left, above and below. A striking example of Mendeleev's success in using the table in this way is his set of predictions concerning the gap in Series 5, Group IV. Group IV contains silicon and elements resembling it. Mendeleev assigned the name "eka-silicon" (Es) to the unknown element. His predictions of the properties of this element are listed in the left-hand column below. In 1887, this element was isolated and identified (it is now called "germanium", Ge); its properties are listed in the right-hand column. Notice how remarkably close Mendeleev's predictions are to the properties actually found.

"The following are the properties which this element should have on the basis of the known properties of silicon, tin, zinc, and arsenic.

Its atomic mass is nearly 72, its forms a higher oxide EsO_2 , . . . Es gives volatile organo-metallic compounds; for instance . . . Es $(\text{C}_2\text{H}_5)_4$, which boils at about 160° , etc.; also a volatile and liquid chloride, EsCl_4 , boiling at about 90° and of specific gravity about 1.9. . . . the specific gravity of Es will be about 5.5, and EsO_2 will have a specific gravity of about 4.7, etc."

The predictions in the left column were made by Mendeleev in 1871. In 1887 an element (germanium) was discovered which was found to have the following properties:

Its atomic mass is 72.5. It forms an oxide GeO_2 , and an organo-metallic compound $\text{Ge}(\text{C}_2\text{H}_5)_4$ which boils at 160° and forms a liquid chloride GeCl_4 which boils at 83°C and has a specific gravity of 1.9. The specific gravity of germanium is 5.5 and the specific gravity of GeO_2 is 4.7.

The daring of Mendeleev is shown in his willingness to venture detailed numerical predictions; the sweep and power of his system is shown above in the remarkable accuracy of those predictions. In similar fashion, Mendeleev described the properties to be expected for the then unknown elements that he predicted to exist in gaps in Group III, period 4, and in Group III, period 5—elements now called gallium and scandium—and again his predictions turned out to be remarkably accurate.

Although not every aspect of Mendeleev's work yielded such successes, these were indeed impressive results, somewhat

reminiscent of the successful use of Newtonian laws to find an unknown planet. Successful numerical predictions like these are among the most desired results in physical science—even if in Mendeleev’s case it was still mysterious why the table should work the way it did.

The discovery of Uranus and Neptune is described in Text Chapter 8.

- Q8** Why is Mendeleev’s table called “periodic table”?
- Q9** What was the basic ordering principle in Mendeleev’s table?
- Q10** What reasons led Mendeleev to leave gaps in the table?
- Q11** What success did Mendeleev have in the use of the table?

17.6 The modern periodic table

The periodic table has had an important place in chemistry and physics for a century. It presented a serious challenge to any theory of the atom proposed after 1880: the challenge that the theory provide an explanation for the wonderful order among the elements as expressed by the table. A successful model of the atom must provide a physical reason why the table works as it does. In Chapter 19 we shall see how one model of the atom—the Bohr model—met this challenge.

Since 1872 many changes have had to be made in the periodic table, but they have been changes in detail rather than in general ideas. None of these changes has affected the basic periodic feature among the properties of the elements. A modern form of the table with current values is shown in the table below.

A modern form of the periodic table of the chemical elements. The number above the symbol is the atomic mass, the number below the symbol is the atomic number.

Group→ Period↓	I	II											III	IV	V	VI	VII	0	
1	1.0080 H 1																		4.0026 He 2
2	6.939 Li 3	9.012 Be 4											10.811 B 5	12.011 C 6	14.007 N 7	15.999 O 8	18.998 F 9	20.183 Ne 10	
3	22.990 Na 11	24.31 Mg 12											26.98 Al 13	28.09 Si 14	30.97 P 15	32.06 S 16	35.45 Cl 17	39.95 Ar 18	
4	39.10 K 19	40.08 Ca 20	44.96 Sc 21	47.90 Ti 22	50.94 V 23	52.00 Cr 24	54.94 M 25	55.85 Fe 26	58.93 Co 27	58.71 Ni 28	63.54 Cu 29	65.37 Zn 30	69.72 Ga 31	72.59 Ge 32	74.92 As 33	78.96 Se 34	79.91 Br 35	83.80 Kr 36	
5	85.47 Rb 37	87.62 Sr 38	88.91 Y 39	91.22 Zr 40	92.91 Nb 41	95.94 Mo 42	(99) Tc 43	101.07 Ru 44	102.91 Rh 45	106.4 Pd 46	107.87 Ag 47	112.40 Cd 48	114.82 In 49	118.69 Sn 50	121.75 Sb 51	127.60 Te 52	126.9 I 53	131.30 Xe 54	
6	132.91 Cs 55	137.34 Ba 56	* 57-71	178.49 Hf 72	180.95 Ta 73	183.85 W 74	186.2 Re 75	190.2 Os 76	192.2 Ir 77	195.09 Pt 78	196.97 Au 79	200.59 Hg 80	204.37 Tl 81	207.19 Pb 82	208.98 Bi 83	210 Po 84	(210) At 85	222 Rn 86	
7	(223) Fr 87	226.05 Ra 88	+ 89-103																
				*Rare-earth metals															
				†Actinide metals															
				138.91 La 57	140.12 Ce 58	140.91 Pr 59	144.27 Nd 60	(147) Pm 61	150.35 Sm 62	151.96 Eu 63	157.25 Gd 64	158.92 Tb 65	162.50 Dy 66	164.93 Ho 67	167.26 Er 68	168.93 Tm 69	173.04 Yb 70	174.97 Lu 71	
				227 Ac 89	232.04 Th 90	231 Pa 91	238.03 U 92	(237) Np 93	(242) Pu 94	(243) Am 95	(245) Cm 96	(249) Bk 97	(249) Cf 98	(253) E 99	(255) Fm 100	(256) Mv 101	(253) No 102	(257) Lw 103	

Although Mendeleev's table had eight columns, the column labelled VIII did not contain a family of elements. It contained the "transition" elements which are now placed in the long series (periods) labelled 4, 5 and 6 in the table on p. 23. The group labelled "O" in that table does consist of a family of elements, the noble gases, which do have similar properties in common.

Helium was first detected in the spectrum of the sun in 1868 (Chapter 19). Its name comes from *helios*, the Greek word for the sun.

In chemistry, elements such as gold and silver that react only rarely with other elements were called "noble."

One difference between the modern and older tables results from new elements having been found. Forty new elements have been identified since 1872, so that the table now contains 103 or more elements. Some of these new elements are especially interesting, and you will learn more about them in Unit 6.

Comparison of the modern form of the table with Mendeleev's table shows that the modern table contains eight groups, or families, instead of seven. The additional group is labeled "zero." In 1894, the British scientists Lord Rayleigh and William Ramsay discovered that about 1 percent of our atmosphere consists of a gas that had previously escaped our detection. It was given the name argon (symbol Ar). Argon does not seem to enter into chemical combination with any other elements, and is not similar to any of the groups of elements in Mendeleev's original table. Later, other elements similar to argon were also discovered: helium (He), neon (Ne), krypton (Kr), xenon (Xe), and radon (Rn). These elements are considered to form a new group or family of elements called the "noble gases." The molecules of the noble gases contain only one atom, and until recent years no compound of any noble gas was known. The group number zero was thought to correspond to the chemical inertness, or zero combining capacity of the members of the group. In 1963, some compounds of xenon and krypton were produced, so we now know that these elements are not really inert. These compounds are not found in nature, however, and some are very reactive, and therefore very difficult to keep. The noble gases as a group are certainly less able to react chemically than any other elements.

In addition to the noble gases, two other sets of elements had to be included in the table. After the fifty-seventh element, lanthanum, room had to be made for a whole set of 14 elements that are almost indistinguishable chemically, known as the *rare earths* or lanthanide series. Most of these elements were unknown in Mendeleev's time. Similarly, after actinium at the eighty-ninth place, there is a set of 14 very similar elements, forming what is called the *actinide* series. These elements are shown in two rows below the main table. No more additions are expected except, possibly, at the end of the table. There are no known gaps, and we shall see in Chapters 19 and 20 that according to the best theory of the atom now available, no new gaps are expected to exist within the table.

Besides the addition of new elements to the periodic table, there have also been some changes of a more general type. As we have seen, Mendeleev arranged most of the elements in order of increasing atomic mass. In the late nineteenth century, however, this basic scheme was found to break down in a few places. For example, the chemical properties of argon (Ar) and potassium (K) demand that they should be placed in the eighteenth and nineteenth positions, whereas on the basis of their atomic masses alone (39.948 for argon, 39.102 for potassium), their positions should be reversed. Other reversals of this kind are also necessary, for example, for the fifty-second element, tellurium (atomic mass = 127.60) and the fifty-third, iodine (atomic mass = 126.90).

The numbers that place elements in the table with the greatest consistency in periodic properties are called the atomic numbers of the elements. The atomic numbers of all the elements are given in the table on p. 23. The atomic number is usually denoted by the symbol Z ; thus for hydrogen, $Z = 1$, for chlorine, $Z = 17$, for uranium, $Z = 92$. In Chapter 19 we shall see that the atomic number has a fundamental physical meaning related to atomic structure, and that is the key to both the many puzzling successes and few puzzling failures of Mendeleev's scheme. Since he used atomic mass as the basis for the order of the elements, he preferred to believe that the apparent reversals were due to error in the values for the atomic masses.

The need for reversals in mass order in the periodic table of the elements was apparent to Mendeleev. He attributed it to faulty atomic weight data. He confidently expected, for example, that the atomic mass of tellurium (which he placed fifty-second), when more accurately determined would turn out to be lower than that of iodine (which he placed fifty-third). And, in fact, in 1872 (see Table p. 20) he had convinced himself that the correct atomic mass of tellurium was 125! As the figures in the modern tables show however, tellurium does have a greater atomic mass than iodine—the reversal is real. Mendeleev overestimated the applicability of the periodic law in every detail, particularly as it had not yet received a physical explanation. He did not realize that atomic mass was not the underlying ordering principle for atomic numbers—it was only one physical property (with slightly imperfect periodicity). Satisfactory explanations for these reversals have been found in modern atomic physics, and will be explained in Unit 6.

SG 17.10–17.12.

Q12 What is the “atomic number” of an element? Give examples of the atomic number of several elements.

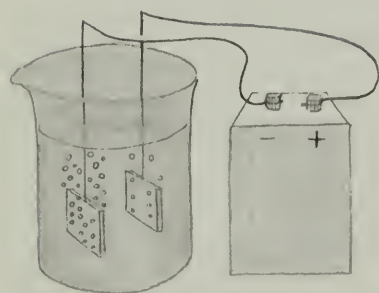
17.7 Electricity and matter: qualitative studies

While chemists were applying Dalton's atomic theory in the first decade of the nineteenth century, another development was taking place which opened an important path to our understanding of the atom. Humphry Davy and Michael Faraday made discoveries which showed that electricity and matter are intimately related. Their discoveries in “electrochemistry” had to do with decomposing chemical compounds by passing an electric current through them. This process is called *electrolysis*.

The study of electrolysis was made possible by the invention of the electric cell in 1800 by the Italian scientist Alessandro Volta. As we saw in Unit 4, Volta's cell consisted of disks of different metals separated from each other by paper moistened with a weak solution of salt. As a result of chemical changes occurring in such a cell, an electric potential difference is established between the metals. A *battery* is a set of several similar cells connected together. A battery usually has two terminals, one charged positively and the other

Some liquids conduct electricity. Pure distilled water is a poor conductor; but when certain substances such as acids or salts are dissolved in water, the resulting solutions are good electrical conductors. Gases are not conductors under normal conditions, but can be made electrically conducting in the presence of strong electric fields, or by other methods. The conduction of electricity in gases, vital to the story of the atom, will be discussed in Chapter 18.

charged negatively. When the terminals are connected to each other by means of wires or other conducting materials, there is an electric current in the battery and the materials. Thus, the battery can produce and maintain an electric current. It is not the only device that can do so, but it was the first source of steady currents.



Humphry Davy (1778–1829) was the son of a farmer. In his youth he worked as an assistant to a physician, but was discharged because of his liking for explosive chemical experiments. He became a chemist, discovered nitrous oxide (laughing gas), which was later used as an anaesthetic, and developed a safety lamp for miners as well as an arc light. His work in electrochemistry and his discovery of several elements made him world-famous; he was knighted in 1812. In 1813 Sir Humphry Davy hired a young man, Michael Faraday, as his assistant and took him along on an extensive trip through France and Italy. It became evident to Davy that young Faraday was a man of scientific genius. Davy is said to have been envious, at first, of Faraday's great gifts. He later said that he believed his greatest discovery was Faraday.

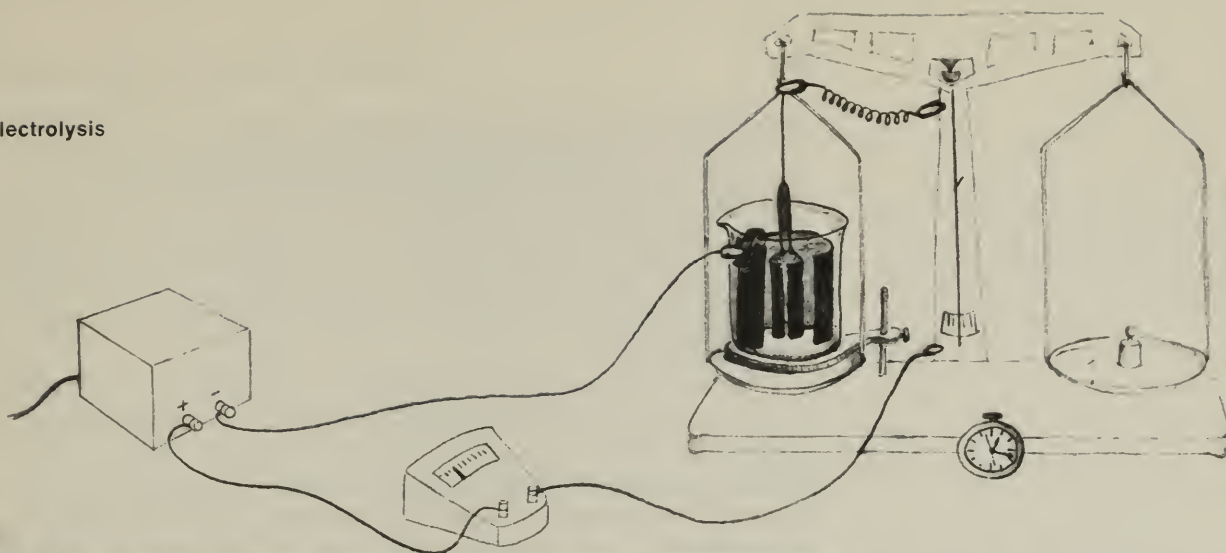
Within a few weeks after Volta's announcement of his discovery it was found that water could be decomposed into oxygen and hydrogen by the use of electric currents. At the left is a diagram of an electrolysis apparatus. The two terminals of the battery are connected, by conducting wires, to two thin sheets of platinum ("electrodes"). When these platinum sheets are immersed in ordinary water, bubbles of oxygen appear at one sheet and bubbles of hydrogen at the other. Adding a small amount of certain acids speeds up the reaction without changing the products. Hydrogen and oxygen gases are formed in the proportion of 7.94 grams of oxygen to 1 gram of hydrogen, which is exactly the proportion in which these elements combine to form water. Water had previously been impossible to decompose, and had long been regarded as an element. Thus the ease with which water was separated into its elements by electrolysis dramatized the chemical use of electricity, and stimulated many other investigations of electrolysis.

Among these investigations, some of the most successful were those of the young English chemist Humphry Davy. Perhaps the most striking of Davy's successes were those he achieved in 1807 when he studied the effect of the current from a large electric battery upon soda and potash. Soda and potash were materials of commercial importance (for example, in the manufacture of glass, soap, and gunpowder) and had been completely resistant to every earlier attempt to decompose them. Soda and potash were thus regarded as true chemical elements—up to the time of Davy's work. (See Dalton's symbols for the elements on p. 10.) When electrodes connected to a large battery were touched to a solid lump of soda, or to a lump of potash, part of the solid was heated to its melting point. At one electrode small globules of molten metal appeared which burned brightly and almost explosively in air. When the electrolysis was done in the absence of air, the metallic material could be collected and studied. The metallic elements discovered in this way were called sodium and potassium. Sodium was obtained from soda (now called sodium hydroxide), and potassium was obtained from potash (now called potassium hydroxide). In the immediately succeeding years, electrolysis experiments made on several previously undecomposed "earths" yielded the first samples ever obtained of such metallic elements as magnesium, strontium, and barium. There were also many other demonstrations of the striking changes produced by the chemical activity of electricity.

Q13 Why was the first electrolysis of water such a surprising achievement?

Q14 What were some other unexpected results of electrolysis?

Electrolysis



(a)



(b)



(c)

Student laboratory apparatus like that shown in the sketch above can be used for experiments in electrolysis. This setup allows measurement of the amount of electric charge passing through the solution in the beaker, and of the mass of metal deposited on the suspended electrode.

The separation of elements by electrolysis is important in industry, particularly in the production of aluminum. These photographs show the large scale of a plant where aluminum is obtained from aluminum ore in electrolytic tanks.

(a) A row of tanks where aluminum is separated out of aluminum ore.

(b) A closer view of the front of some tanks, showing the thick copper straps that carry the current for electrolysis.

(c) A huge vat of molten aluminum that has been siphoned out of the tanks is poured into molds.

By chemical change we mean here the breaking up of molecules during electrolysis, as by gas bubbles rising at the electrodes, or by metal deposited on it.

17.8 Electricity and matter: quantitative studies

Davy's work on electrolysis was mainly qualitative. But quantitative questions were also asked. How much chemical change can be produced when a certain amount of electric charge is passed through a solution? If the same amount of charge is passed through different solutions, how do the amounts of chemical change compare? Will doubling the amount of electricity double the chemical change effected?

The first answers to these questions were obtained by Michael Faraday, who discovered two fundamental and simple empirical laws of electrolysis. He studied the electrolysis of a solution of the blue salt copper sulfate in water. The electric current between electrodes placed in the solution caused copper from the solution to be deposited on the negative electrode and oxygen to be liberated at the positive electrode. Faraday determined the amount of copper deposited on the cathode by weighing the cathode before the electrolysis started and again after a known amount of current had passed through the solution. He found that the mass of copper deposited depends on only two things: the magnitude of the electric current (measured, say, in amperes), and the length of time that the current was maintained. In fact, the mass of copper deposited is directly proportional to both the current and the time. When either was doubled, the mass of copper deposited was doubled. When both were doubled, four times as much copper was deposited. Similar results were found in experiments on the electrolysis of many different substances.

Faraday's results may be described by stating that the amount of chemical change produced in electrolysis is proportional to the product of the current and the time. Now, the current (in amperes) is the quantity of charge (in coulombs) transferred per unit time (in seconds). The product of current and time therefore gives the *total charge* in coulombs that has moved through the cell during the given experiment. We then have Faraday's first law of electrolysis:

$$\text{Mass} \propto \frac{\text{current} \times \text{time}}{\text{charge transferred}}$$

The mass of an element liberated at an electrode during electrolysis is proportional to the amount of charge which has passed through the electrode.

Next Faraday measured the mass of different elements liberated from chemical compounds by equal amount of electric charge. He found that the amount of an element liberated from the electrolyte by a given amount of electricity depends on the element's *atomic mass* and on its combining capacity (valence). His second law of electrolysis states:

This experimentally determined amount of electric charge, 96,540 coulombs, is now called a *faraday*.

If A is the atomic mass of an element, and if v is its valence, a transfer of 96,540 coulombs of electric charge liberate A/v grams of the element.

**Masses of elements that would be electrolyzed from compounds by
96,540 coulombs of electric charge.**

ELEMENT	ATOMIC MASS A	COMBINING CAPACITY v	MASS OF ELEMENT LIBERATED (grams)
Hydrogen	1.008	1	1.008
Chlorine	35.45	1	35.45
Oxygen	16.00	2	8.00
Copper	63.54	2	31.77
Zinc	65.37	2	32.69
Aluminum	26.98	3	8.99

The values of atomic mass in this table are based on a value of exactly 16 for oxygen.

law of electrolysis. In each case the mass of the element produced by electrolysis is equal to its atomic mass divided by its combining capacity.

The quantity A/v was recognized to have significance beyond just electrolysis experiments. For example, the values for A/v are 8.00 for oxygen and 1.008 for hydrogen. The ratio is $8.00/1.008 = 7.94$. But as we have found before, this is just the ratio of masses of oxygen and hydrogen that combine to produce water. In general, when two elements combine, the ratio of their combining masses is equal to the ratio of their values for A/v .

Faraday's second law of electrolysis has an important implication. It shows that a given amount of electric charge is somehow closely connected with the atomic mass and valence of an element. The mass and valence are characteristic of the atoms of the element. Perhaps, then, a certain amount of electricity is somehow connected with an *atom* of the element. The implication is that electricity may also be atomic in character. This possibility was considered by Faraday, who wrote cautiously:

... if we adopt the atomic theory or phraseology, then the atoms of bodies which are equivalents to each other in their ordinary chemical action have equal quantities of electricity naturally associated with them. But I must confess that I am jealous of the term *atom*; for though it is very easy to talk of atoms, it is very difficult to form a clear idea of their nature, especially when compound bodies are under consideration.

In Chapter 18 you will read about the details of the research that did establish the fact that electricity itself is atomic in character, and that the "atoms" of electricity are part of the atoms of matter. This research, for which Faraday's work and his cautious guess prepared, helped make possible the exploration of the structure of the atom.

SG 17.17–17.20

Q15 The amount of an element deposited in electrolysis depends on three factors. What are they?

Q16 What are the significances of the quantity A/v for an element?

17.1 The Project Physics learning materials particularly appropriate for Chapter 17 include the following:

Experiment

Electrolysis

Activities

Dalton's Puzzle

Electrolysis of Water

Periodic Table

Single-electrode Plating

Activities from the Scientific American

Film Loops

Production of Sodium by Electrolysis

Articles of general interest in *Reader 5* are:

The Island of Research

The Sentinel

Although most of the articles in *Reader 5* are related to ideas presented in Chapter 20, you may prefer to read some of them earlier.

17.2 The chemical compound zinc oxide (molecular formula ZnO) contains equal numbers of atoms of zinc and oxygen. Using values of atomic masses from the modern version of the periodic table (on page 23), find the percentage by mass of zinc in zinc oxide. What is the percentage of oxygen in zinc oxide?

17.3 The chemical compound zinc chloride (molecular formula ZnCl_2) contains two atoms of chlorine for each atom of zinc. Using values of atomic masses from the modern version of the periodic table, find the percentage by mass of zinc in zinc chloride.

17.4 During the complete decomposition of a 5.00-gram sample of ammonia gas into its component elements, nitrogen and hydrogen, 4.11 grams of nitrogen were obtained. The molecular formula of ammonia is NH_3 . Find the mass of a nitrogen atom relative to that of a hydrogen atom. Compare your result with the one you would get by using the values of the atomic masses in the modern version of the periodic table. If your result is different from the latter result, how do you account for the difference?

17.5 From the information in Problem 17.3, calculate how much nitrogen and hydrogen are needed to make 1.2 kg of ammonia.

17.6 If the molecular formula of ammonia were falsely thought to be NH_2 , and you used the result of the experiment in Problem 17.3, what value would you get for the ratio of the mass of a nitrogen atom relative to that of a hydrogen atom?

17.7 A sample of nitric oxide gas, weighing 1.00 g, after separation into its components, is found to have contained 0.47 g of nitrogen. Taking the atomic mass of oxygen to be 16.00, find the corresponding numbers that express the atomic mass of nitrogen relative to oxygen on the respective assumptions that the molecular formula of nitric oxide is (a) NO ; (b) NO_2 ; (c) N_2O .

17.8 Early data yielded 8.2/8.0 for the mass ratio of nitrogen and oxygen atoms, and 1/7 for the mass ratio of hydrogen and oxygen atoms. Show that these results lead to a value of 6 for the relative atomic mass of nitrogen, provided that the value 1 is assigned to hydrogen.

17.9 Given the molecular formulae HCl , NaCl , CaCl_2 , AlCl_3 , SnCl_4 , PCl_5 , find possible combining capacities of sodium, calcium, aluminum, tin and phosphorus.

17.10 (a) Examine the modern periodic table of elements and cite all reversals of order of increasing atomic mass.

(b) Restate the periodic law in your own words, not forgetting about these reversals.

17.11 On the next page is a table of the melting and boiling temperatures of the elements.

(a) Plot these quantities against atomic number in two separate graphs. Comment on any periodicity you observe in the plots.

(b) Predict the values for melting and boiling points of the noble gases, which were unknown in 1872. Compare your predictions with the modern values given in, say, the *Handbook of Chemistry and Physics*.

17.12 In recent editions of the *Handbook of Chemistry and Physics* there are printed in or below one of the periodic tables the valence numbers of the elements. Neglect the negative valence numbers and plot (to element 65) a graph of maximum valences observed vs. atomic mass. What periodicity is found? Is there any physical or chemical significance to this periodicity?

17.13 According to the table on p. 29, when about 96,500 coulombs of charge pass through a water solution, how much of oxygen will be released at the same time when (on the other electrode) 1.008 g of hydrogen are released? How much oxygen will be produced when a current of 3 amperes is passed through water for 60 minutes (3600 seconds)?

17.14 If a current of 0.5 amperes is passed through molten zinc chloride in an electrolytic apparatus, what mass of zinc will be deposited in

(a) 5 minutes (300 seconds);

(b) 30 minutes;

(c) 120 minutes?

17.15 (a) For 20 minutes (1200 seconds), a current of 2.0 amperes is passed through molten zinc chloride in an electrolytic apparatus. What mass of chlorine will be released at the anode?

- (b) If the current had been passed through molten zinc iodide rather than molten zinc chloride what mass of iodine would have been released at the anode?
- (c) Would the quantity of zinc deposited in part (b) have been different from what it was in part (a)? Why?
- (d) How would you set up a device for plating a copper spoon with silver?

17.16 What may be the relation of Faraday's speculation about an "atom of electricity" to the presumed atomicity in the composition of chemical elements?

17.17 96,540 coulombs in electrolysis frees A grams of a monovalent element of atomic mass A such as hydrogen when hydrochloric acid is used as electrolyte. How much chlorine will be released on the other electrode?

17.18 If 96,540 coulombs in electrolysis always frees A grams of a monovalent element, A/2 grams of a divalent element, etc., what relation does this suggest between valence and "atoms" of electricity?

17.19 The idea of chemical elements composed of identical atoms makes it easier to correlate the phenomena discussed in this chapter. Could the phenomena be explained without using the idea of atoms? Are chemical phenomena, which usually involve a fairly large quantity of material (in terms of the number of "atoms"), sufficient evidence for Dalton's belief that an element consists of atoms, all of which are exactly identical with each other?

17.20 A sociologist recently wrote a book about the place of man in modern society, called *Multivalent Man*. In general, what validity is there for using such terms for sociological or other descriptions?

17.21 Which of Dalton's main postulates (pp. 11-12) were similar to those in Greek atomism (pp. 4-5)? Which are quite different?

Melting and Boiling Temperatures of the Elements Known by 1872

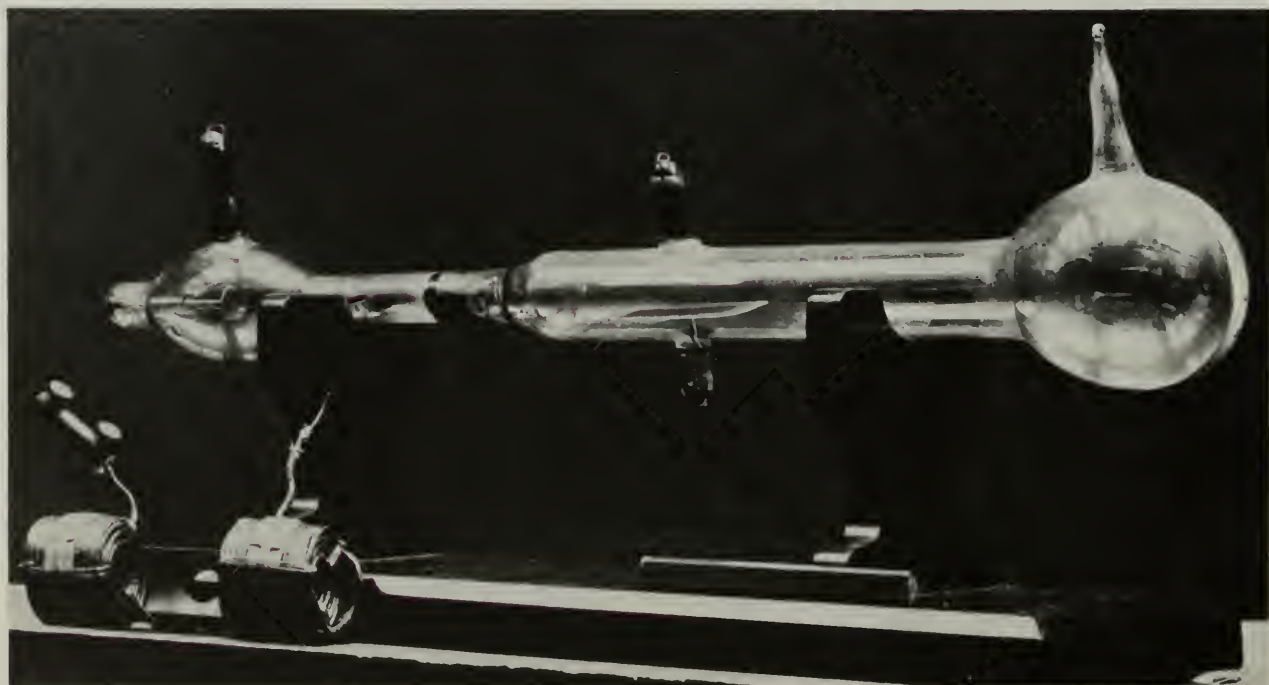
ATOMIC NUMBER	NAME	MELTING POINT	BOILING POINT
1	hydrogen	-259°C	-253°C
3	lithium	186	1340
4	beryllium	1280	2970
5	boron	2300	2550
6	carbon	>3350	4200
7	nitrogen	-210	-196
8	oxygen	-218	-183
9	fluorine	-223	-188
11	sodium	98	880

Melting and Boiling Temperatures of the Elements Known by 1872 (cont.)

ATOMIC NUMBER	NAME	MELTING POINT	BOILING POINT
12	magnesium	651	1107
13	aluminum	660	2057
14	silicon	1420	2355
15	phosphorus	44	280
16	sulfur	113	445
17	chlorine	-103	-35
19	potassium	62	760
20	calcium	842	1240
22	titanium	1800	>3000
23	vanadium	1710	3000
24	chromium	1890	2480
25	manganese	1260	1900
26	iron	1535	3000
27	cobalt	1495	2900
28	nickel	1455	2900
29	copper	1083	2336
30	zinc	419	907
33	arsenic	814	615
34	selenium	217	688
35	bromine	-7	59
37	rubidium	39	700
38	strontium	774	1150
39	yttrium	1490	2500
40	zirconium	1857	>2900
41	niobium	2500	3700
42	molybdenum	2620	4800
44	ruthenium	2450	2700
45	rhodium	1966	2500
46	palladium	1549	2200
47	silver	961	1950
48	cadmium	321	767
49	indium	156	2000
50	tin	232	2270
51	antimony	631	1380
52	tellurium	452	1390
53	iodine	114	184
55	cesium	29	670
56	barium	725	1140
57	lanthanum	826
58	cerium	804	1400
68	erbium
73	tantalum	3000	4100
74	tungsten	3370	5900
76	osmium	2700	>5300
77	iridium	2454	>4800
78	platinum	1774	4300
79	gold	1063	2600
80	mercury	-39	357
81	thallium	302	1460
82	lead	327	1620
83	bismuth	271	1560
90	thorium	1845	4500
92	uranium	1133	ignites

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The tube used by J. J. Thomson to determine the charge-to-mass ratio of electrons.



CHAPTER EIGHTEEN

Electrons and Quanta

18.1 The idea of atomic structure

The successes of chemistry in the nineteenth century, in accounting for combining proportions and in predicting chemical reactions, had proved to the satisfaction of most scientists that matter is composed of atoms.

But there remained a related question: are atoms really indivisible, or do they consist of still smaller particles? We can see the way in which this question arose by thinking a little more about the periodic table. Mendeleev had arranged the elements in the order of increasing atomic mass. But the atomic masses of the elements cannot explain the *periodic* features of Mendeleev's table. Why, for example, do the 3rd, 11th, 19th, 37th, 55th, and 87th elements, with quite different atomic masses, have similar chemical properties? Why are these properties somewhat different from those of the 4th, 12th, 20th, 38th, 56th, and 88th elements in the list, but greatly different from the properties of the 2nd, 10th, 18th, 36th, 54th, and 86th elements?

The periodicity in the properties of the elements led to speculation about the possibility that atoms might have structure, that they might be made up of smaller pieces. The gradual changes of properties from group to group might suggest that some unit of atomic structure is added, in successive elements, until a certain portion of the structure is completed. The completed condition would occur in the atom of a noble gas. In an atom of the next heavier element, a new portion of the structure may be started, and so on. The methods and techniques of classical chemistry could not supply experimental evidence for such structure. In the nineteenth century, however, discoveries and new techniques in physics opened the way to the proof that atoms do, indeed, consist of smaller pieces. Evidence piled up that suggested the atoms of different elements differ in the number and arrangement of these pieces.

In this chapter, we shall discuss the discovery of one structural element which all atoms contain: the electron. Then we shall see how experiments with light and electrons led to a revolutionary

SG 18.1

These elements burn when exposed to air; they decompose water, often explosively.

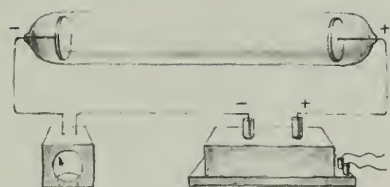
These elements react slowly with air or water.

These elements rarely combine with any others.

idea – that *light* energy is transmitted in discrete amounts. In Chapter 19, we shall describe the discovery of another part of the atom, the nucleus. Finally we shall show how Niels Bohr combined these pieces to create a workable model of the atom. The story starts with the discovery of cathode rays.

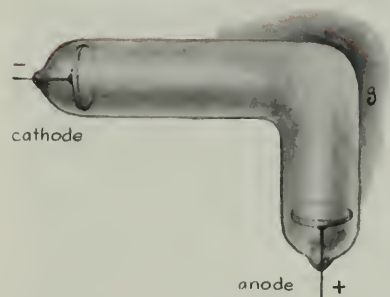
18.2 Cathode rays

In 1855 the German physicist Heinrich Geissler invented a vacuum pump which could remove enough gas from a strong glass tube to reduce the pressure to 0.01 percent of normal air pressure. It was the first major improvement in vacuum pumps after Guericke's invention of the air pump, two centuries earlier. It turned out to be a critical technical innovation that opened new fields to pure scientific research. Geissler's friend Julius Plücker connected one of Geissler's evacuated tubes to a battery. He was surprised to find that at the very low pressure that could be obtained with Geissler's pump, electricity flowed through the tube. Plücker used apparatus similar to that sketched in the margin. He sealed a wire into each end of a strong glass tube. Inside the tube, each wire ended in a metal plate, called an electrode. Outside the tube, each wire ran to a source of high voltage. (The negative plate is called the *cathode*, and the positive plate is called *anode*.) A meter indicated the current in the tube.



Cathode ray apparatus

Substances which glow when exposed to light are called fluorescent. Fluorescent lights are essentially Geissler tubes with an inner coating of fluorescent powder.



Bent Geissler tube. The most intense green glow appeared at g



A Crookes tube

Plücker and his student, Johann Hittorf, noticed that when an electric current passes through the low-pressure gas in a tube, the tube itself glows with a pale green color. Several other scientists observed these effects, but two decades passed before anyone undertook a thorough study of the glowing tubes. By 1875, Sir William Crookes had designed new tubes for studying the glow produced when an electric current passes through an evacuated tube. When he used a bent tube, (see figure at the left) the most intense green glow appeared on the part of the tube which was directly opposite the cathode (at g). This suggested that the green glow was produced by something which comes out of the cathode and travels down the tube until it hits the glass. Another physicist, Eugen Goldstein, who was studying the effects of passing an electric current through a gas at low pressure, named whatever it was that appeared to be coming from the cathode, *cathode rays*. For the time being, it was quite mysterious just what these cathode rays were.

To study the nature of the rays, Crookes did some ingenious experiments. He reasoned that if cathode rays could be stopped before they reached the end of the tube, the intense green glow would disappear. He therefore introduced barriers (for example, in the form of a Maltese cross, as in the sketch in the margin). A shadow of the barrier appeared in the midst of the green glow at the end of the tube. The cathode seemed to act like a source which radiates a kind of light; the cross acted like a barrier blocking the light. Because the shadow, cross, and cathode appeared along one straight line, Crookes concluded that the cathode rays, like light rays, travel in straight lines. Next, Crookes moved a magnet near

the tube, and the shadow moved. Thus he found that magnetic fields deflected the paths of cathode rays (which does not happen with light).

In the course of many experiments, Crookes found the following properties of cathode rays:

- (a) No matter what material the cathode is made of, it produces rays with the same properties.
- (b) In the absence of a magnetic field, the rays travel in straight lines perpendicular to the surface that emits them.
- (c) A magnetic field deflects the path of the cathode rays.
- (d) The rays can produce some chemical reactions similar to the reactions produced by light; for example, certain silver salts change color when hit by the rays.

In addition, Crookes suspected (but did not succeed in showing) that (e) charged objects deflect the path of cathode rays.

Physicists were fascinated by the cathode rays. Some thought that the rays must be a form of light, because they have so many of the properties of light: they travel in straight lines, and produce chemical changes and fluorescent glows just as light does. According to Maxwell's theory of electricity and magnetism, light consists of electromagnetic waves. So the cathode rays might, for example, be electromagnetic waves of frequency much higher than that of visible light.

However, magnetic fields do not bend light; they do bend the path of cathode rays. In Chapter 14 we described how magnetic fields exert forces on currents, that is, on moving electric charges. Since a magnetic field deflects cathode rays in the same way that it deflects negative charges, some physicists believed that cathode rays consisted of negatively charged particles.

The controversy over whether cathode rays are a force of electromagnetic waves or a stream of charged particles continued for 25 years. Finally, in 1897, J. J. Thomson made a series of experiments which convinced physicists that the cathode rays are negatively charged particles. Details of Thomson's experiment and calculations are given on page 36.

It was then well-known that the paths of charged particles are affected by both magnetic and electric fields. By assuming that the cathode rays were negatively charged particles, Thomson could predict what should happen to the cathode rays when they passed through such fields. For example, it should be possible to balance the deflection of a beam of cathode rays by a magnetic field by turning on an electric field of just the right magnitude and direction. As page 36 indicates, the predictions were verified, and Thomson could therefore conclude that the cathode rays were indeed made up of negatively charged particles. He was then able to calculate, from the experimental data, the ratio of the charge of a particle to its mass. This ratio is denoted by q/m , where q is the charge and m is the mass of the particle.

Thomson found that the rays coming from cathodes made of different materials all had the same value of q/m , namely 1.76×10^{11} coulombs per kilogram.

J. J. Thomson later observed this to be possible.



Sir Joseph John Thomson (1856–1940), one of the greatest British physicists, attended Owens College in Manchester, England and then Cambridge University. He worked on the conduction of electricity through gases, on the relation between electricity and matter and on atomic models. His greatest single contribution was the discovery of the electron. He was the head of the famous Cavendish Laboratory at Cambridge University, where one of his students was Ernest Rutherford.

Thomson's q/m Experiment

J. J. Thomson measured the ratio of charge q to mass m for cathode-ray particles by means of the evacuated tube shown in the photograph on page 32. A high voltage applied between two electrodes in the left end of the tube produced cathode rays. Those rays that passed through both slotted cylinders in the narrow neck of the tube formed a nearly parallel beam. The beam produced a spot of light on a fluorescent coating inside the large end of the tube at the right.



The path of the beam was deflected by an electric field applied between two horizontal plates in the mid-section of the tube; (note that direction of electric field \vec{E} is upward along plane of page):

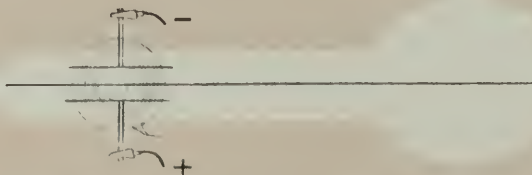


The beam's path was also deflected when there was no electric field but when a magnetic field was set up by means of a pair of current-carrying wire coils placed around the midsection of the tube; (the direction of the magnetic field \vec{B} is into the plane of the page):



When only the magnetic field \vec{B} is turned on, particles in the beam, having charge q and speed v , would experience a force Bqv ; because the force is always perpendicular to the direction of the velocity vector, the beam would be deflected in a nearly circular arc of radius R as long as it is in the nearly uniform magnetic field. If the particles in the beam have mass m , they must be experiencing a centripetal force mv^2/R while moving in a circular arc. Since the centripetal force is provided by the magnetic force Bqv , we can write $Bqv = mv^2/R$. Rearranging terms: $q/m = v/BR$.

B can be calculated from the geometry of the coils and the electric current in them. R can be found geometrically from the displacement of the beam spot on the end of the tube. To determine v , Thomson applied the electric field and the magnetic field at the same time, and arranged the directions and strengths of the two fields so that the electric field \vec{E} exerted a downward force Eq on the beam particles exactly equal to the upward force Bqv due to the magnetic field—as seen by the fact that the beam, acted on by both fields in opposing ways, goes along a straight line.



If the magnitudes of the forces due to the electric and magnetic fields are equal, then $Eq = Bqv$. Solving for v we have: $v = E/B$. E can be calculated from the separation of the two plates and the voltage between them; so the speed of the particles v can be determined. Now all the terms on the right of the earlier equation for q/m are known, and q/m can be computed.

Thus, it was clear that cathode rays must be made of something all materials have in common. Thomson's negatively charged particles were later called *electrons*. The value of q/m for the cathode ray particles was about 1800 times larger than the values of q/m for hydrogen ions, 9.6×10^7 coulombs per kilogram as measured in electrolysis experiments of the kind we discussed in Sec. 17.8. (See table on p. 29.) Thomson concluded from these results that either the *charge* of the cathode ray particles is much greater than that of the hydrogen ion, or the *mass* of the cathode ray particles is much less than the mass of the hydrogen ion.

SG 18.2

Thomson also made measurements of the charge q on these negatively charged particles with methods other than those involving deflection by electric and magnetic fields. Although these experiments were not very accurate, they were good enough to indicate that the charge of a cathode ray particle was the same or not much different from that of the hydrogen ion in electrolysis. In view of the small value of q/m , Thomson was therefore able to conclude that the mass of cathode ray particles is much less than the mass of hydrogen ions.

In short, the cathode ray particles, or electrons, were found to have two important properties: (1) they were emitted by a wide variety of cathode materials, and (2) they were much smaller in mass than the hydrogen atom, which has the smallest known mass. Thomson therefore concluded that the cathode ray particles form a part of all kinds of matter. He suggested that the atom is not the ultimate limit to the subdivision of matter, and that the electron is part of an atom, that it is, perhaps even a basic building block of atoms. We now know that this is correct: the electron—whose existence Thomson had first proved by quantitative experiment—is one of the fundamental or “elementary” particles of which matter is made.

In the article in which he published his discovery, Thomson also speculated on the ways in which such particles might be arranged in atoms of different elements, in order to account for the periodicity of the chemical properties of the elements. Although, as we shall see in the next chapter, he did not say the *last* word about the arrangement and number of electrons in the atom, he did say the *first* word about it.

Q1 What was the most convincing evidence that cathode rays were not electromagnetic radiation?

Q2 What was the reason given for the ratio q/m for electrons being 1800 times larger than q/m for hydrogen ions?

Q3 What were two main reasons for Thomson's belief that electrons may be “building blocks” from which all atoms are made?

18.3 The measurement of the charge of the electron: Millikan's experiment

After the ratio of charge to the mass (q/m) of the electron had been determined, physicists tried to measure the value of the

charge q itself in a variety of ways. If the charge could be determined, the mass of the electron could be found from the known value of q/m . In the years between 1909 and 1916, the American physicist Robert A. Millikan succeeded in measuring the charge of the electron. This quantity is one of the fundamental constants of physics; it comes up again and again in atomic and nuclear physics as well as in electricity and electromagnetism.

Millikan's "oil-drop experiment" is still one of the nicest experiments that students can do, and is described in general outline on page 39. He found that the electric charge that a small object such as an oil drop can pick up is always a simple multiple of a certain *minimum value*. For example, the charge may have the value -4.8×10^{-19} coulombs, or -1.6×10^{-19} coulombs, or -6.4×10^{-19} coulombs, or -1.6×10^{-18} coulombs. But it never has a charge of, say, -2.4×10^{-19} coulombs, and it never has a value smaller than -1.6×10^{-19} coulombs. In other words, electric charges always come in multiples (1, 2, 3 . . .) of 1.6×10^{-19} coulombs, a quantity often symbolized by q_e . Millikan took this minimum charge to be the amount of charge of a single electron.

SG 18.3

The magnitude of the charge of nuclei or atomic and molecular ions has also turned out always to come in multiples of the electron charge q_e . For example, when a chemist refers to a "doubly charged oxygen ion," he means that the magnitude of the charge of the ion is $2q_e$, or 3.2×10^{-19} coulombs.

Note that Millikan's experiments did not prove that no charges smaller than q_e can exist. All we can say is that no experiment has yet proved the existence of smaller charges. There are recent theoretical reasons to expect that in some very high-energy experiments, another elementary particle of charge of $\frac{1}{3} q_e$ may eventually be discovered; but no such "fractional" charge is expected to be found on nuclei, ions, or droplets.

In everyday life, the electric charge one meets is so large compared to that on one electron that one can think of such charges or currents as being continuous—just as one usually thinks of the flow of water in a river as continuous rather than as a flow of individual molecules. A current of one ampere, for example, is equivalent to the flow of 6.25×10^{18} electrons per second. The "static" electric charge one accumulates by shuffling over a rug on a dry day consists of something like 10^{12} electron charges.

Since the work of Millikan, a wide variety of other experiments involving many different fields within physics have all pointed to the same basic unit of charge as being fundamental in the structure and behavior of atoms, nuclei, and particles smaller than these. For example, it has been shown directly that cathode ray particles carry this basic unit of charge—that they are, in other words, electrons.

By combining Millikan's value for the electron charge q_e with Thomson's value for the ratio of charge to mass (q_e/m), we can calculate the mass of a single electron (see margin). The result found is that the mass of the electron is about 10^{-30} kilograms. From electrolysis experiments (see Sec. 17.8) we know that the

From now on we denote the magnitude of the charge of the electron by q_e :

$$q_e = 1.6 \times 10^{-19} \text{ coul.}$$

The sign of the charge is negative for the electron.

In 1964, an American physicist, Murray Gell-Mann, suggested that particles with charge equal to $1/3$ or $2/3$ of q_e might exist. He named these particles "quarks"—the word comes from James Joyce's novel *Finnegan's Wake*. Quarks are now being looked for in cosmic-ray and bubble-chamber experiments.

Thomson found that

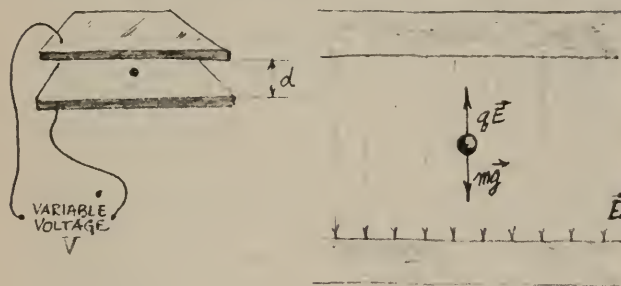
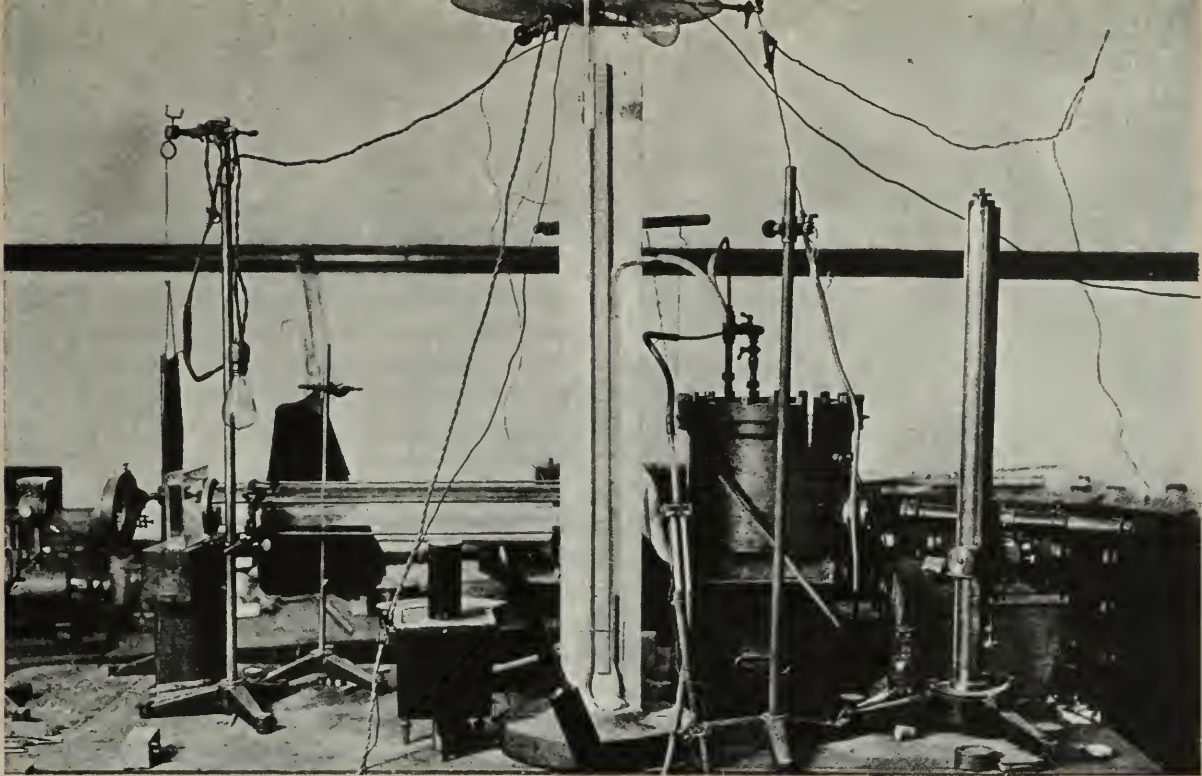
$$q_e/m = 1.76 \times 10^{11} \text{ coul/kg.}$$

According to Millikan's experiment the magnitude of q_e is 1.6×10^{-19} coul.

Therefore, the mass of an electron is:

$$m = \frac{1.6 \times 10^{-19} \text{ coul}}{1.76 \times 10^{11} \text{ coul/kg}} \\ = 0.91 \times 10^{-30} \text{ kg}$$

(Mass of a hydrogen ion is 1.66×10^{-27} kg. This is approximately the value of one "atomic mass unit.")



Millikan's Oil-drop Experiment

R. A. Millikan's own apparatus (about 1910) for measuring the charge of the electron is seen in the photograph above. A student version of Millikan's apparatus shown in the lower photograph was taken in a laboratory period of the Projects Physics Course.

In principle Millikan's experiment is simple; the essential part of the apparatus is sketched above. When oil is sprayed into the chamber containing two horizontal plates, the minute droplets formed are electrically charged as they emerge from the spray nozzle. The charge of a droplet is what must be measured. Consider a small oil drop of mass m carrying an electric charge q . It is situated between the two horizontal plates that are separated by a distance d and at an electrical potential difference V . There will be a uniform electric field \vec{E} between the plates, of strength V/d (see Sec. 14.8). This field can be adjusted so that the electrical force $q\vec{E}$ exerted upward

on the drop's charge will balance the force ma_g exerted downward by gravity. In this balanced situation,

$$F_{el} = F_{grav}$$

therefore

$$qE = ma_g$$

or

$$q = ma_g/E$$

The mass of the drop can, in principle, be determined from its radius and the density of the oil from which it was made. Millikan had to measure these quantities by an indirect method, but it is now possible to do the experiment with small manufactured polystyrene spheres instead of oil drops. Their mass is known, so that some of the complications of the original experiment can be avoided. Millikan's remarkable result was that the charge q on objects such as an oil drop is always a multiple (1, 2, 3 . . .) times a smallest charge, which he identified with the charge of one electron (q_e).

charge-to-mass ratio of a hydrogen ion is 1836 times smaller than the charge-to-mass ratio of an electron. Since an electron and a hydrogen ion form a neutral hydrogen atom when they combine, it is reasonable to expect that they have equal and opposite charges. We may therefore conclude that the mass of the hydrogen ion is 1836 times as great as the mass of the electron: that is the mass of the hydrogen ion is $1836 \times 0.91 \times 10^{-30} \text{ kg} = 1.66 \times 10^{-27} \text{ kg}$. This is approximately the value of one *atomic mass unit*.

Q4 Oil drops pick up different amounts of electric charge. On what basis did Millikan decide that the lowest charge he found was actually just one electron charge?

18.4 The photoelectric effect

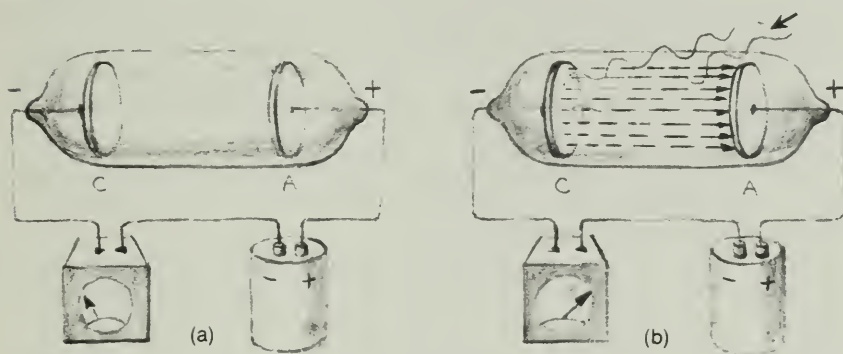
In 1887 the German physicist Heinrich Hertz was testing Maxwell's theory of electromagnetic waves. He noticed that a metallic surface can emit electric charges when light of very short wavelength falls on it. Because light and electricity are both involved, the name *photoelectric effect* was given to this phenomenon. When the electric charges so produced passed through electric and magnetic fields, the direction of their paths was changed in the same rays as the path of cathode rays. It was therefore deduced that the electric charges consist of negatively charged particles. In 1898, J. J. Thomson measured the value of the ratio q/m for these photoelectrically emitted particles with the same method that he used for the cathode ray particles. He got the same value for the particles ejected in the photoelectric effect as he had earlier for the cathode-ray particles. By means of these experiments (and others) the photoelectric particles were shown to have the same properties as electrons. In fact, we must consider them to be ordinary electrons, although they are often referred to as *photoelectrons*, to indicate their origin. Later work showed that all substances, solids, liquids and gases, exhibit the photoelectric effect under appropriate conditions. It is, however, convenient to study the effect with metallic surfaces.

The photoelectric effect, which we shall be studying in greater detail, has had an important place in the development of atomic physics. The effect could not be explained in terms of the ideas of physics we have studied so far. New ideas had to be introduced to account for the experimental results. In particular, a revolutionary concept was introduced—that of *quanta*. A new branch of physics—*quantum theory*—developed at least in part because of the explanation provided for the photoelectric effect.

The basic information for studying the photoelectric effect comes from two kinds of measurements: measurements of the *photoelectric current* (the number of photoelectrons emitted per unit time); and measurements of the *kinetic energies* with which the photoelectrons are emitted.

The *photoelectric current* can be studied with an apparatus like that sketched in Fig. (a) in the margin. Two metal plates, C and A, are sealed inside a well-evacuated quartz tube. (Quartz glass is transparent to ultraviolet light as well as visible light.) The two plates are connected to a source of potential difference (for example, a battery). In the circuit is also an ammeter. As long as light strikes plate C, as in Fig. (b), electrons are emitted from it. If the potential of plate A is positive relative to plate C, these emitted photoelectrons will accelerate to plate A. (Some emitted electrons will reach plate A even if it is not positive relative to C.) The resulting “photoelectric” current is indicated by the ammeter. The result of the experiment is that the stronger the beam of light of a given color (frequency), the greater the photoelectric current.

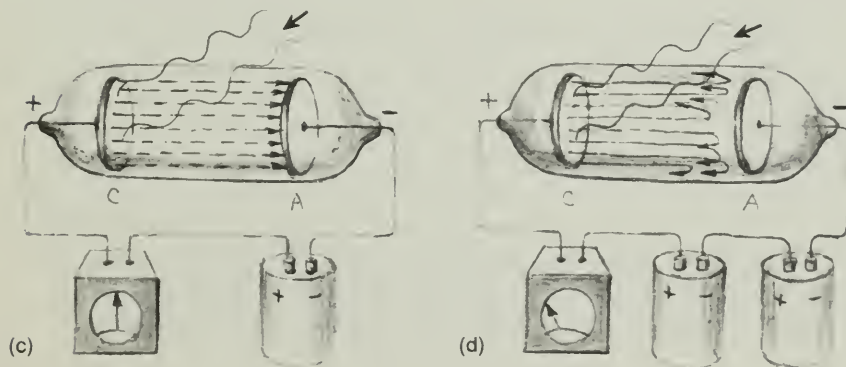
The best way to study this part—as most other parts—of physics is really by doing the experiments discussed!



Schematic diagram of apparatus for photoelectric experiments.

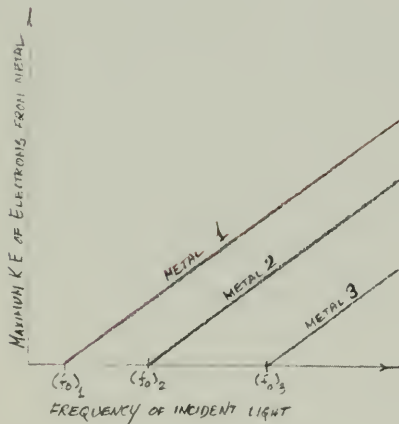
Any metal used as the plate C shows a photoelectric effect, but only if the light has a frequency *greater* than a certain value. This value of the frequency is called the *threshold frequency* for that metal. Different metals have different threshold frequencies. If the incident light has a frequency lower than the threshold frequency, *no* photoelectrons are emitted, no matter how great the intensity of the light is or how long the light is left on! This is the first of a set of surprising discoveries.

The *kinetic energies of the electrons* can be measured in a slightly modified version of the apparatus, sketched in Fig. (c) below. The battery is reversed so that the plate A now tends to repel the photoelectrons. The voltage can be changed from zero to a value just large enough to keep any electrons from reaching the plate A, as indicated in Fig. (d).



SG 18.4

In Sec. 14.8, we saw that the change in potential energy of a charge is given by Vxq . In Unit 3 we saw that (in the absence of friction) the decrease in kinetic energy in a system is equal to the increase in its potential energy.



Photoelectric effect: maximum kinetic energy of the electrons as a function of the frequency of the incident light; different metals yield lines that are parallel, but have different threshold frequencies.

When the voltage across the plates is zero, the meter will indicate a current, showing that the photoelectrons emerge from the metallic surface with kinetic energy and so can reach plate A. As the repelling voltage is increased the photoelectric current decreases until a certain voltage is reached at which the current becomes zero, as indicated in Fig. (d) above. This voltage, which is called the *stopping voltage*, is a measure of the maximum kinetic energy of the emitted photoelectrons (KE_{max}). If the stopping voltage is denoted by V_{stop} , this maximum kinetic energy is given by the relation:

$$KE_{max} = V_{stop} q_e$$

The results may be stated more precisely. For this purpose let us now number the important experimental results to make it more convenient to discuss their theoretical interpretation later.

(1) A substance shows a photoelectric effect only if the incident light radiation has a frequency above a certain value called the threshold frequency (symbol f_0).

(2) If light of a given frequency does produce a photoelectric effect, the photoelectric current from the surface is proportional to the intensity of the light falling on it.

(3) If light of a given frequency liberates photoelectrons, the emission of these electrons is *immediate*. The time interval between the incidence of the light on the metallic surface and the appearance of electrons has been found to be at most 3×10^{-9} sec. and is probably much less. In some experiments, the light intensity used was so low that, according to the classical theory, it should take several hundred seconds for an electron to accumulate enough energy from the light to be emitted. But even in these cases electrons are sometimes emitted about a billionth of a second after the light strikes the surface.

(4) The maximum kinetic energy of the photoelectrons increases in direct proportion to the frequency of the light which causes their emission, and is independent of the intensity of the incident light. The way in which the maximum kinetic energy of the electrons varies with the frequency of the incident light is shown in the margin where the symbols $(f_0)_1$, $(f_0)_2$ and $(f_0)_3$ stand for the different threshold frequencies of three different substances. For each substance, the experimental data points fall on a straight line. All the lines have the same slope.

What is most astonishing about the results is that photoelectrons are emitted if the light frequencies are a *little above* the threshold frequency, no matter how weak the beam of light is; but if the light frequencies are just a *bit below* the threshold frequency, no electrons are emitted *no matter how great the intensity of the light beam is*.

Findings (1), (3) and (4) could not be explained on the basis of the classical electromagnetic theory of light. There was no way in which a low-intensity train of light waves spread out over a large number of atoms could, in a very short time interval, concentrate

enough energy on one electron to knock the electron out of the metal.

Furthermore, the classical wave theory was unable to account for the existence of a threshold frequency. There seemed to be no reason why a sufficiently intense beam of low-frequency radiation would not be able to produce photoelectricity, if low-intensity radiation of higher frequency could produce it. Similarly, the classical theory was unable to account for the fact that the maximum kinetic energy of the photoelectrons increases linearly with the frequency of the light but is independent of the intensity. Thus, the photoelectric effect posed a challenge which the classical wave theory of light could not meet.

Q5 Light falling on a certain metal surface causes electrons to be emitted. What happens to the photoelectric current as the intensity of the light is decreased?

Q6 What happens as the frequency of the light is decreased?

Q7 Sketch a rough diagram of the equipment and circuit used to demonstrate the main facts of photoelectricity.

18.5 Einstein's theory of the photoelectric effect

The explanation of the photoelectric effect was the major work cited in the award to Albert Einstein of the Nobel Prize in physics for the year 1921. Einstein's theory, proposed in 1905, played a major role in the development of atomic physics. The theory was based on a daring proposal. Not only were most of the experimental details still unknown in 1905, but the key point of Einstein's explanation was contrary to the classical ideas of the time.

Einstein assumed that energy of light is not distributed evenly over the whole expanding wave front (as is assumed in the classical theory), but rather remains concentrated in separate "lumps." Further, the amount of energy in each of these regions is not just any amount, but a definite amount of energy which is proportional to the frequency f of the wave. The proportionality factor is a constant, denoted by h , and is called Planck's constant, for reasons which will be discussed later. Thus, in this model, the light energy in a beam of frequency f comes in pieces, each of amount $h \times f$. The amount of radiant energy in each piece is called a *quantum* of energy. It represents the smallest quantity of energy of light of that frequency. The quantum of light energy was later called a *photon*.

There is no explanation clearer or more direct than Einstein's. We quote from his first paper (1905) on this subject, changing only the notation used there to make it coincide with usual current practice (including our own notation):

... According to the idea that the incident light consists of quanta with energy hf , the ejection of cathode rays by light can be understood in the following way. Energy

See the articles "Einstein" and "Einstein and some Civilized Discontents" in *Reader 5*.

$$h = 6.6 \times 10^{-34} \text{ joule-sec}$$

SG 18.5

Each electron must be given a minimum energy to emerge from the surface because it must do work against the forces of attraction as it leaves the rest of the atoms.

This equation is usually called Einstein's photoelectric equation.

quanta penetrate the surface layer of the body, and their energy is converted, at least in part, into kinetic energy of electrons. The simplest picture is that a light quantum gives up all its energy to a single electron; we shall assume that this happens. The possibility is not to be excluded, however, that electrons receive their energy only in part from the light quantum. An electron provided with kinetic energy inside the body may have lost part of its kinetic energy by the time it reaches the surface. In addition, it is to be assumed that each electron, in leaving the body, has to do an amount of work W (which is characteristic of the body). The electrons ejected directly from the surface and at right angles to it will have the greatest velocities perpendicular to the surface. The maximum kinetic energy of such an electron is

$$KE_{max} = hf - W$$

If the body plate C is charged to a positive potential, V_{stop} just large enough to keep the body from losing electric charge, we must have

$$KE_{max} = hf - W = V_{stop} q_e$$

where q_e is the magnitude of the electronic charge . . .

If the derived formula is correct, then V_{stop} , when plotted as a function of the frequency of the incident light, should yield a straight line whose slope should be independent of the nature of the substance illuminated.

SG 18.6-18.8.

How Einstein's theory explains the photoelectric effect:

- (1) No photoelectric emission below threshold frequency. Reason: low-frequency photons don't have enough energy to provide electrons with KE sufficient to leave the metal.
- (2) Current \propto light intensity. Reason: one photon ejects one electron.

SG 18.9, 18.10

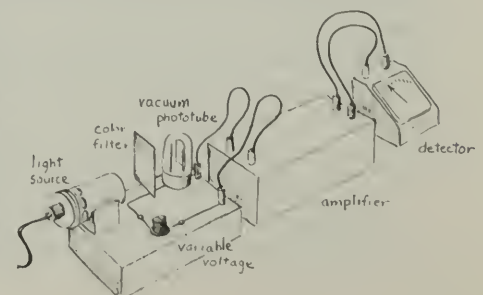


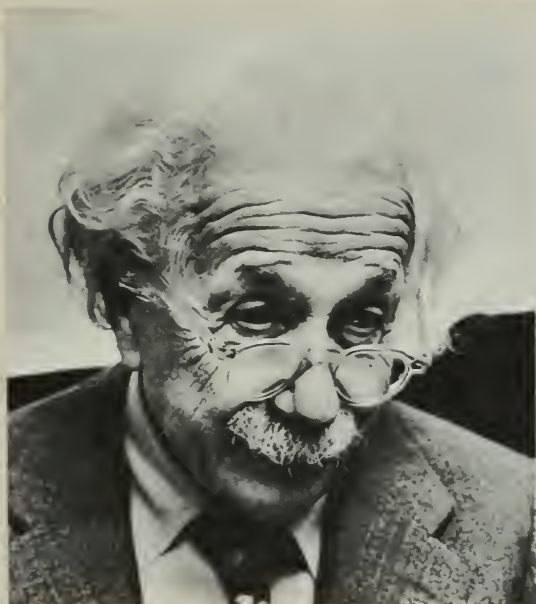
We can now compare Einstein's photoelectric equation with the experimental results to test whether or not his theory accounts for the results. According to the equation, the kinetic energy is greater than zero only when hf is greater than W . Hence, the equation says that an electron can be emitted only when the frequency of the incident light is greater than a certain lowest value f_0 (where $hf_0 = W$.)

Next, according to Einstein's photon model, it is an individual photon that ejects an electron. The intensity of the light is proportional to the number of the photons in the light beam, and the number of photoelectrons ejected is proportional to the number of photons incident on the surface. Hence the number of electrons ejected (and with it the photoelectric current) is proportional to the intensity of the incident light.

According to Einstein's model the light energy is concentrated in the quanta (photons). So, no time is needed for collecting light

Student apparatus for photoelectric experiments often includes a vacuum phototube, like the one shown at the left. The collecting wire corresponds to A in Fig. (a) on p. 41, and is at the center of a cylindrical photosensitive surface that corresponds to C. The frequency of the light entering the tube is selected by placing colored filters between the tube and a white light source, as shown at the right.





Albert Einstein (1879-1955) was born in the city of Ulm, in Germany. Like Newton he showed no particular intellectual promise as a youngster. He received his early education in Germany, but at the age of 17, dissatisfied with the regimentation in school and militarism in the nation, he left for Switzerland. After graduation from the Polytechnic School, Einstein (in 1901) found work in the Swiss Patent Office in Berne. This job gave Einstein a salary to live on and an opportunity to use his spare time for working in physics on his own. In 1905 he published three papers of epoch-making importance. One dealt with quantum theory and included his theory of the photoelectric effect. Another treated the problem of molecular motions and sizes, and worked out a mathematical analysis of the phenomenon of "Brownian motion." Einstein's analysis and experimental work by Jean Perrin, a French physicist, provided a strong argument for the molecular motions assumed in the kinetic theory. Einstein's third 1905 paper provided the theory of special relativity which revolutionized modern thought about the nature of space, time, and physical theory.



In 1915, Einstein published a paper on the theory of general relativity in which he provided a new theory of gravitation that included Newton's theory as a special case.

When Hitler and the Nazis came to power in Germany, in 1933, Einstein came to the United States and became a member of the Institute for Advanced Studies at Princeton. He spent the rest of his working life seeking a unified theory which would include gravitation and electromagnetics. Near the beginning of World War II, Einstein wrote a letter to President Roosevelt, warning of the war potential of an "atomic bomb," for which the Germans had all necessary knowledge and motivation to work. After World War II, Einstein devoted much of his time to promoting world agreement to end the threat of atomic warfare.

(3) Immediate emission. Reason: a single photon provides the energy concentrated in one place.

(4) KE_{max} increases linearly with frequency above f_0 . Reason: the work needed to remove the electron is $W = hf_0$; any energy left over from the original photon is now available for kinetic energy of the electron.

energy; the quanta transfer their energy immediately to the photoelectrons, which emerge after the very short time required for them to escape from the surface.

Finally, the photoelectric equation predicts that the greater the frequency of the incident light, the greater is the maximum kinetic energy of the ejected electrons. According to the photon model, the photon's energy is directly proportional to the light frequency. The minimum energy needed to eject an electron is the energy required for the electron to escape from the metal surface—which explains why light of frequency less than some frequency f_0 cannot eject any electrons. The kinetic energy of the escaping electron is the difference between the energy of the absorbed photon and the energy lost by the electron in passing through the surface.

Thus, Einstein's photoelectric equation agreed qualitatively with the experimental results. There remained two quantitative tests to be made: (1) does the maximum energy vary in direct proportion to the light frequency? (2) is the proportionality factor h really the same for all substances? For some 10 years, experimental physicists attempted these quantitative tests. One of the experimental difficulties was that the value of W for a metal is greatly changed if there are impurities (for example, a layer of oxidized metal) on the surface. It was not until 1916 that it was established, by Robert A. Millikan, that there is indeed a straight-line relationship between the frequency of the absorbed light and the maximum kinetic energy of the photoelectrons (as in the graph on p. 42). To obtain his data Millikan designed an apparatus in which the metal photoelectric surface was cut clean while in a vacuum. A knife inside the evacuated volume was manipulated by an electromagnet outside the vacuum to make the cuts. This rather intricate arrangement was required to achieve an uncontaminated metal surface.

Millikan also showed that the straight line graphs obtained for different metals all had the same slope, even though the threshold frequencies were different. The value of h could be obtained from Millikan's measurements; it was the same for each metal surface, and, it agreed very well with a value obtained by means of other, independent methods. So Einstein's theory of the photoelectric effect was verified quantitatively.

Historically, the first suggestion that the energy in electromagnetic radiation is "quantized" (comes in definite quanta) came not from the photoelectric effect, but from studies of the heat and light radiated by hot solids. The concept of *quanta of energy* was introduced by Max Planck, a German physicist, in 1900, five years before Einstein's theory, and the constant h is known as *Planck's constant*. Planck was trying to account for the way heat (and light) energy radiated by a hot body is related to the frequency of the radiation. Classical physics (nineteenth-century thermodynamics and electromagnetism) could not account for the experimental facts. Planck found that the facts could be interpreted only by assuming that atoms, on radiating, change their energy discontinuously, in quantized amounts. Einstein's theory of the photoelectric effect was actually an extension and application of Planck's quan-

The equation $KE_{max} = hf - W$ can be said to have led to two Nobel prizes: one to Einstein, who derived it theoretically, and one to Millikan, who verified it experimentally. This equation is the subject of a Project Physics laboratory experiment.

SG 18.11



Robert Andrews Millikan (1868-1953), an American physicist, attended Oberlin College, where his interest in physics was only mild. After his graduation he became more interested in physics, taught at Oberlin while taking his master's degree, and then obtained his doctor's degree from Columbia University in 1895. After post-doctoral work in Germany he went to the University of Chicago, where he became a professor of physics in 1910. His work on the determination of the electronic charge took place from 1906 to 1913. He was awarded the Nobel Prize in physics in 1923 for this research, and for the very careful experiments which resulted in the verification of the Einstein photoelectric equation (Sec. 18.4). In 1921, Millikan moved to the California Institute of Technology, eventually to become its president.

tum theory of thermal radiation: Einstein postulated that the quantum change in the atom's energy is carried off as a localized photon rather than being spread continuously over the light wave.

The experiments and the theory on radiation are much more difficult to describe than the experiments and the theory of the photoelectric effect. That is why we have chosen to introduce the new concept of quanta of energy by means of the photoelectric effect. By now, there have been many ways of checking both Planck's and Einstein's conceptions. In all these cases, Planck's constant h has now the same basic position in quantum physics that Newton's universal constant G has in the physics of gravitation.

The photoelectric effect presented physicists with a real dilemma. According to the classical wave theory, light consists of electromagnetic waves extending continuously throughout space. This theory was highly successful in explaining optical phenomena (reflection, refraction, polarization, interference), but could not account for the photoelectric effect. Einstein's theory, in which the existence of separate lumps of light energy was postulated, accounted for the photoelectric effect; it could not account for the other properties of light. The result was that there were two models whose basic concepts seemed to be mutually contradictory. Each model had its successes and failures. The problem was: what, if anything, could be done about the contradictions between the two models? We shall see later that the problem and its treatment have a central position in modern physics.



Max Planck (1858-1947), a German physicist, was the originator of the quantum theory, one of the two great revolutionary physical theories of the 20th century. (The other is Einstein's relativity theory.) Planck won the Nobel Prize in 1918 for his quantum theory. He tried for many years to show that this theory can be understood in terms of the classical physics of Newton and Maxwell, but this attempt did not succeed. Quantum physics is fundamentally different, through its postulate that energy in light and matter is not continuously divisible into any arbitrarily small quantity, but exists in quanta of definite amount.

Q8 Einstein's idea of a quantum of light had a definite relation to the wave model of light. What was it?

Q9 Why does the photoelectron not have as much energy as the quantum of light which causes it to be ejected?



Wilhelm Konrad Röntgen (1845-1923)

Q10 What does a “stopping voltage” of, say, 2.0 volts indicate about the photoelectrons emerging from a metal surface?

18.6 X rays

In 1895, a surprising discovery was made which, like the photoelectric effect, did not fit in with accepted ideas about electromagnetic waves and eventually needed quanta for its explanation. The discovery was that of x rays by the German physicist, Wilhelm Röntgen; its consequences for atomic physics and technology are dramatic and important.

On November 8, 1895, Röntgen was experimenting with the newly found cathode rays, as were many physicists all over the world. According to a biographer,

... he had covered the all-glass pear-shaped tube [Crookes tube—see Sec. 18.2] with pieces of black cardboard, and had darkened the room in order to test the opacity of the black paper cover. Suddenly, about a yard from the tube, he saw a weak light that shimmered on a little bench he knew was nearby. Highly excited, Röntgen lit a match and, to his great surprise, discovered that the source of the mysterious light was a little barium platinocyanide screen lying on the bench.

Barium platinocyanide, a mineral, is one of the many chemicals known to *fluoresce*, that is, to emit visible light when illuminated with ultraviolet light. But no source of ultraviolet light was present in Röntgen’s experiment. Cathode rays had not been observed to travel more than a few centimeters in air. So, neither ultraviolet light nor the cathode rays themselves could have caused the fluorescence. Röntgen therefore deduced that the fluorescence he had observed was due to rays of a new kind, which he named *x rays*, that is, rays of an unknown nature. During the next seven weeks he made a series of experiments to determine the properties of this new radiation. He reported his results on December 28, 1895 to a scientific society in a paper whose title (translated) is “On a New Kind of Rays.”

Röntgen’s paper described nearly all of the properties of x rays that are known even now. It included an account of the method of producing the rays, and proof that they originated in the glass wall of the tube, where the cathode rays struck it. Röntgen showed that the x rays travel in straight lines from their place of origin and that they darken a photographic plate. He reported in detail the ability of x rays to penetrate various substances—paper, wood, aluminum, platinum and lead. Their penetrating power was greater through light materials (paper, wood, flesh) than through dense materials (platinum, lead, bone). He described photographs showing “the shadows of bones of the hand, of a set of weights inside a small box, and of a piece of metal whose inhomogeneity becomes apparent with x rays.” He gave a clear description of the shadows

The discovery of x rays was narrowly missed by several physicists, including Hertz and Lenard (another well-known German physicist). An English physicist, Frederick Smith, found that photographic plates kept in a box near a cathode-ray tube were liable to be fogged—so he told his assistant to keep them in another place!

Opposite: One of the earliest x-ray photographs made in the United States (1896). The man x-rayed had been hit by a shotgun blast.



Michael J. Dempsey
Columbia University

cast by the bones of the hand on the fluorescent screen. Röntgen also reported that the x rays were not deflected by a magnetic field, and showed no reflection, refraction or interference effects in ordinary optical apparatus.

X rays were often referred to as Röntgen rays, after their discoverer.

It is easy to see why a charged electroscope will be discharged when the air around it is ionized: It attracts the ions of the opposite charge from the air.

One of the most important properties of x rays was discovered by J. J. Thomson a month or two after the rays themselves had become known. He found that when the rays pass through a gas they make it a conductor of electricity. He attributed this effect to “a kind of electrolysis, the molecule being split up, or nearly split up by the Röntgen rays.” The x rays, in passing through the gas, knock electrons loose from some of the atoms or molecules of the gas. The atoms or molecules that lose these electrons become positively charged. They are called ions because they resemble the positive ions in electrolysis, and the gas is said to be *ionized*. The freed electrons may also attach themselves to previously neutral atoms or molecules, thereby leaving them negatively charged.

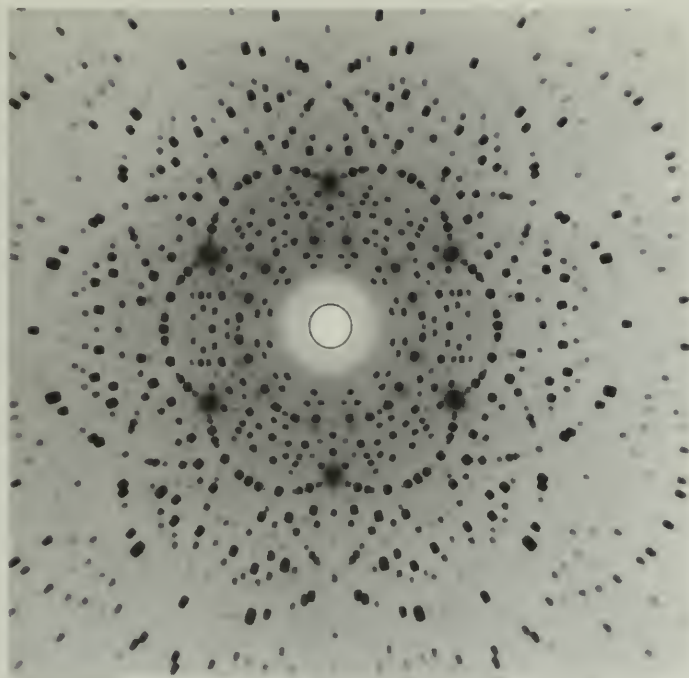
Röntgen and Thomson found, independently, that electrified bodies are discharged when the air around them is ionized by x rays. The rate of discharge was shown to depend on the intensity of the rays. This property was therefore used as a convenient quantitative means of measuring the intensity of an x-ray beam. As a result, careful quantitative measurements of the properties and effects of x rays could be made.

Such a particle—the neutron—was discovered in 1932. You will see in Chapter 23 (Unit 6) how hard it was to identify. But the neutron has nothing to do with x rays.

One of the problems that aroused keen interest during the years following the discovery of x rays was that of the nature of the mysterious rays. They did not act like charged particles—electrons for example—because they were not deflected by magnetic or electric fields. Therefore it seemed that they had to be either neutral particles or electromagnetic waves. It was difficult to choose between these two possibilities. On the one hand, no neutral particles of atomic size (or smaller) were then known which had the penetrating power of x rays. The existence of neutral particles with high penetrating power would be extremely hard to prove in any case, because there was no way of getting at them. On the other hand, if the x rays were electromagnetic waves, they would have to have *extremely short wavelengths*: only in this case, according to theory, could they have high penetrating power and show no refraction or interference effects with ordinary optical apparatus.

SG 18.12

As we have already discussed in Chapters 12 and 13, distinctly wavelike properties become apparent only when waves interact with objects (like slits in a barrier) that are smaller than several wavelengths across. The wavelength hypothesized for x rays would be on the order of 10^{-10} meter. So to demonstrate their wave behavior, it would be necessary to see, say, a diffraction grating with slits spaced about 10^{-10} meter apart. Several lines of evidence, from kinetic theory and from chemistry, indicated that atoms were about 10^{-10} meter in diameter. It was suggested, therefore, that x rays might be diffracted noticeably by crystals, in which the atoms are arranged in orderly layers about 10^{-10} meter apart. In 1912, such experiments succeeded; the layers of atoms do act like



X-ray diffraction patterns from a metal crystal. The black spots are produced by constructive interference of x rays.

diffraction gratings, and x rays do, indeed, act like electromagnetic radiations of very short wavelength—like *ultra* ultraviolet light. These experiments are more complicated to interpret than diffraction of a beam of light by a single, two-dimensional optical grating. Now the diffraction effect occurs in three dimensions instead of two. Hence the diffraction patterns are far more elaborate (see the illustration above).

SG 18.13

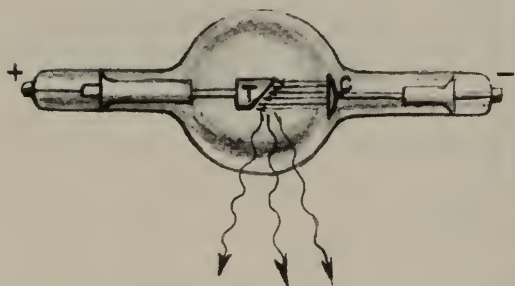
In addition to wave properties, x rays were also found to have quantum properties: they can, for example, cause the emission of electrons from metals. These electrons have greater kinetic energies than those produced by ultraviolet light. (The ionization of gases by x rays is also an example of the photoelectric effect; in this case the electrons are freed from the atoms and molecules of the gas.) Thus, x rays also require quantum theory for the explanation of some of their behavior. So, like light, x rays were shown to have both wave and particle properties.

SG 18.14–18.16

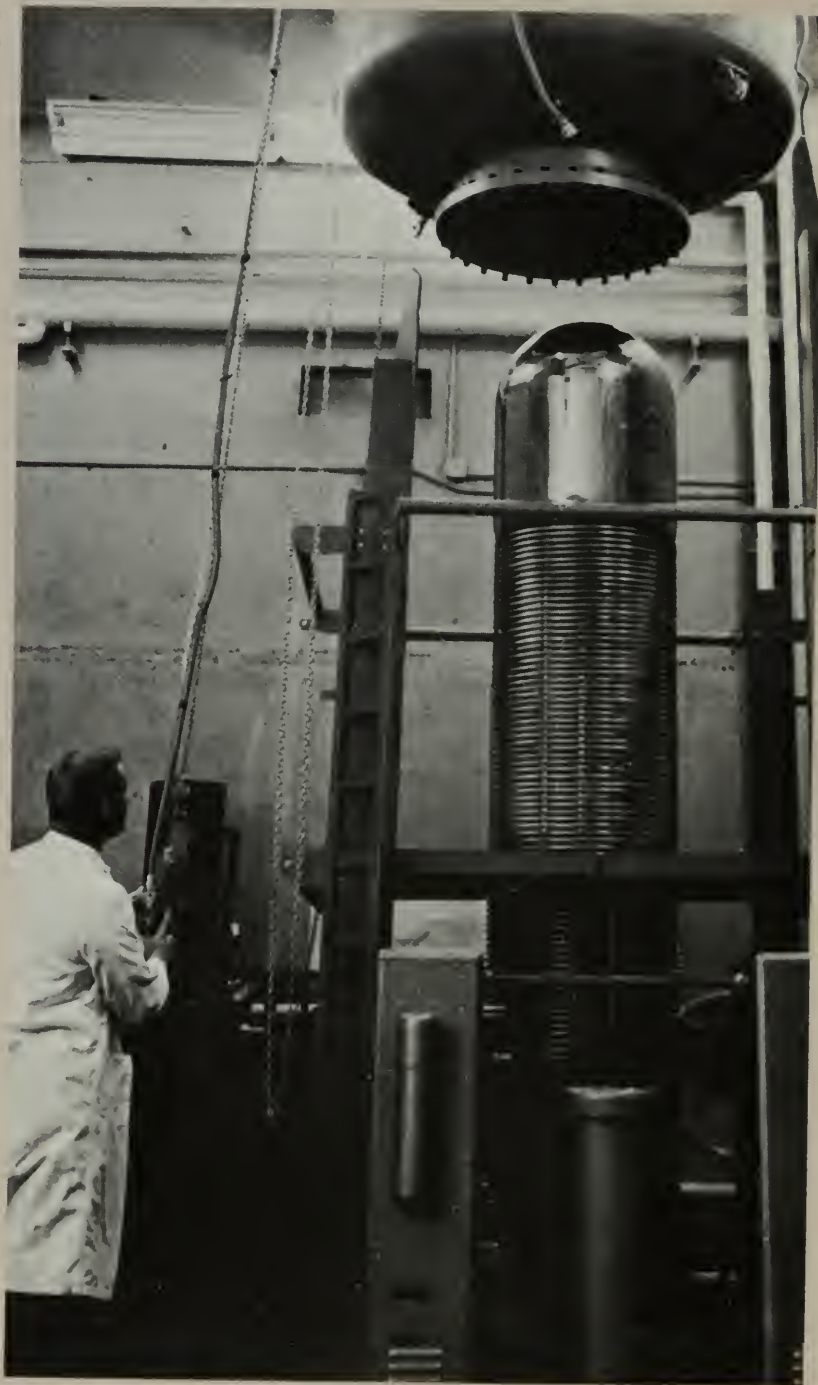
Röntgen's initial discovery of x rays excited intense interest throughout the entire scientific world. His experiments were immediately repeated—and extended in many laboratories in both Europe and America. The scientific journals during the year 1896 were filled with letters and articles describing new experiments or confirming the results of earlier experiments. (This widespread experimentation was made possible by the fact that, during the years before Röntgen's discovery, the passage of electricity through gases had been a popular topic for study by physicists—many physics laboratories had cathode-ray tubes, and could produce x rays easily.)

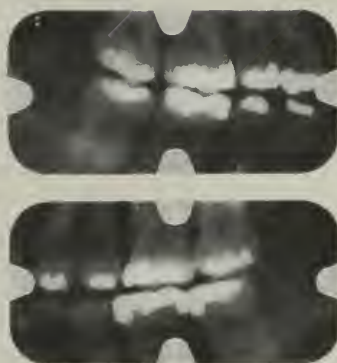
Intense interest in x rays was generated by the spectacular use of these rays in medicine. Within three months of Röntgen's

Originally, x rays were produced in Röntgen's laboratory when cathode rays (electrons) struck a target (the glass wall of the tube). Nowadays x rays are commonly produced by directing a beam of high energy electrons onto a metal target. As the electrons are deflected and stopped, x rays of various energies are produced. The maximum energy a single ray can have is the total kinetic energy the incident electron is giving up on being stopped. So the greater the voltage across which the electron beam is accelerated, the more energetic—and penetrating—are the x rays. One type of x ray tube is shown in the sketch below, where a stream of electrons is emitted from a cathode C and accelerated to a tungsten target T by a strong electric field (high potential difference).



In the photograph at the right is the inner part of a high voltage generator which can be used to provide the large potential differences required for making energetic x rays. This Van de Graaf type generator (named after the American physicist who invented it), although not very different in principle from the electrostatic generators of the 18th century, can produce an electric potential difference of 4,000,000 volts between the top and ground.





Above left is a rose, photographed with x rays produced when the potential difference between the electron-emitting cathode and the target in the x-ray tube is 30,000 volts.

Below the rose is the head of a dogfish shark; its blood vessels have been injected with a fluid that absorbs x rays in order to study the blood vessels.

In the photograph at the bottom of the page, x rays are being used to inspect the welds of a 400-ton tank for a nuclear reactor.

Immediately above is illustrated the familiar use of x rays in dentistry and the resulting records. Because x rays are injurious to tissues, a great deal of caution is required in using them. For example, the shortest possible pulse of x rays is used, lead shielding is provided for the body, and the technician stands behind a wall of lead and lead glass.



discovery, x rays were being put to practical use in a hospital in Vienna in connection with surgical operations. The use of this new aid to surgery spread rapidly. Since Röntgen's time, x rays have revolutionized some phases of medical practice, especially the diagnosis of some diseases, and the treatment of some forms of cancer. In other fields of applied science, both physical and biological, uses have been found for x rays which are nearly as important as their use in medicine. Among these are the study of the crystal structure of materials; "industrial diagnosis," such as the search for possible defects in materials and engineering structures; the study of old paintings and sculptures; and many others.

Q11 X rays were the first "ionizing" radiation discovered. What does "ionizing" mean?

Q12 What were three properties of x rays that led to the conclusion that x rays were electromagnetic waves?

Q13 What was the evidence that x rays had a very short wavelength?

18.7 Electrons, quanta and the atom

By the beginning of the twentieth century enough chemical and physical information was available so that many physicists devised models of atoms. It was known that negative particles with identical properties—electrons could be obtained from many different substances and in different ways. This suggested the notion that electrons are constituents of all atoms. But electrons are negatively charged, while samples of an element are ordinarily electrically *neutral* and the atoms making up such samples are also presumably neutral. Hence the presence of negative electrons in an atom would seem to require the presence also of an equal amount of positive charge.

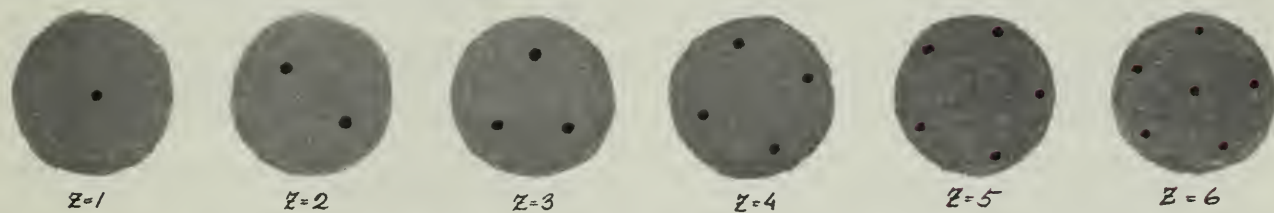
Comparison of the values of q/m for the electron and for charged hydrogen atoms indicated, as mentioned in Sec. 18.2, that hydrogen atoms are nearly two thousand times more massive than electrons. Experiments (which will be discussed in some detail in Chapter 22) showed that electrons constitute only a very small part of the atomic mass in any atom. Consequently any model of an atom must take into account the following information: (a) an electrically neutral atom contains equal amounts of positive and negative charge; (b) the negative charge is associated with only a small part of the mass of the atom. Accordingly, any atomic model should answer at least two questions: (1) how *many* electrons are there in an atom, and (2) how are the electrons and the positive charge *arranged* in an atom?

During the first ten years of the twentieth century, several atomic models were proposed, but none was satisfactory. The early models were all based entirely upon classical physics, that is, upon the physics of Newton and Maxwell. No one knew how to invent a model that also took account of the theory of Planck which

incorporated the quantization of energy. There was also need for more detailed experimental facts—for example, this was the period during which the charge on the electron and the main facts of photoelectricity were still being found. Nevertheless physicists cannot and should not wait until every last fact is in—that will never happen, and you can't even know what the missing facts *are* unless you have some sort of model. Even an incomplete or a partly wrong model will provide clues on which to build a better one.

Until 1911 the most popular model for the atom was one proposed by J. J. Thomson in 1904. Thomson suggested that an atom consisted of a sphere of positive electricity in which was distributed an equal amount of negative charge in the form of electrons. Under this assumption, the atom was like a pudding of positive electricity with the negative electricity scattered in it like raisins. The positive “fluid” was assumed to act on the negative charges, holding them in the atom by means of electric forces only. Thomson did not specify how the positive “fluid” was held together. The radius of the atom was taken to be of the order of 10^{-10} m, on the basis of information from the kinetic theory of gases and other considerations (see SG 18.13). With this model Thomson was able to calculate that certain arrangements of electrons would be stable, the first requirements for explaining the existence of stable atoms. Thomson's theory also suggested that chemical properties might be associated with particular groupings of electrons. A systematic repetition of chemical properties might then occur among groups of elements. But it was not possible to deduce the detailed structure of the atoms of particular elements, and no detailed comparison with the actual periodic table could be made.

See the Project Physics film loop
Thomson Model of the Atom.



Some stable (hypothetical) arrangements of electrons in Thomson atoms. The atomic number Z is interpreted as equal to the number of electrons.

In Chapter 19 we shall discuss some additional experimental information that provided valuable clues to improved models of the structure of atoms. We shall also see how one of the greatest physicists of our time, Niels Bohr, was able to combine the experimental evidence then available with the new concept of quanta into a successful theory of atomic structure. Although Bohr's model was eventually replaced by more sophisticated ones, it provided the clues that led to the presently accepted theory of the atom, and to this day is in fact quite adequate for explaining most of the main facts with which we shall be concerned in this course.

Q14 Why was most of the mass of an atom believed to be associated with positive electric charge?

Q15 Why don't physicists wait until “all the facts are in” before they begin to theorize or make models?

18.1 The Project Physics learning materials particularly appropriate for Chapter 18 include the following:

Experiments

The charge-to-mass ratio for an electron
The measurement of elementary charge
The photoelectric effect

Activities

Writings by and about Einstein
Measuring q/m for the electron
Cathode rays in a Crookes tube
X rays from a Crookes tube
Lighting a bulb photoelectrically with a match

Reader Articles

Failure and Success
Einstein

Transparencies

Photoelectric experiment
Photoelectric equation

18.2 In Thomson's experiment on the ratio of charge to mass of cathode ray particles (p. 36), the following might have been typical values for B , V and d : with a magnetic field B alone, the deflection of the beam indicated a radius of curvature of the beam within the field of 0.114 meters for $B = 1.0 \times 10^{-3}$ tesla.* With the same magnetic field, the addition of an electric field in the same region ($V = 200$ volts, plate separation $d = 0.01$ meter) made the beam go on straight through.

- Find the speed of the cathode ray particles in the beam.
- Find q/m for the cathode ray particles.

18.3 Given the value for the charge on the electron, show that a current of one ampere is equivalent to the movement of 6.25×10^{18} electrons per second past a given point.

18.4 In the apparatus of Fig. 18.7, an electron is turned back before reaching plate A and eventually arrives at electrode C from which it was ejected. It arrives with some kinetic energy. How does this final energy of the electron compare with the energy it had as it left the electrode C?

18.5 It is found that at light frequencies below the threshold frequency no photoelectrons are emitted. What happens to light energy?

18.6 For most metals, the work function W is about 10^{-19} joules. Light of what frequency will cause photoelectrons to leave the metal with virtually no kinetic energy? In what region of the spectrum is this frequency?

18.7 What is the energy of a light photon which

corresponds to a wavelength of 5×10^{-7} m?
 5×10^{-8} m?

18.8 The minimum or threshold frequency of light from emission of photoelectrons for copper is 1.1×10^{15} cycles/sec. When ultraviolet light of frequency 1.5×10^{15} cycles/sec shines on a copper surface, what is the maximum energy of the photoelectrons emitted, in joules? In electron volts?

18.9 What is the lowest-frequency light that will cause the emission of photoelectrons from a surface whose work function is 2.0 eV (that is, an energy of at least 2.0 eV is needed to eject an electron)?

18.10 Monochromatic light of wavelength 5000 Å falls on a metal cathode to produce photoelectrons. ($1 \text{ Å} = 10^{-10}$ meter) The light intensity at the surface of the metal is 10^2 joules/m² per sec.

- What is the frequency of the light?
- What is the energy (in joules) of a single photon of the light?
- How many photons fall on 1 m² in one sec?
- If the diameter of an atom is about 1 Å, how many photons fall on one atom in one second, on the average?
- How often would one photon fall on one atom, on the average?
- How many photons fall on one atom in 10^{-10} sec, on the average?
- Suppose the cathode is a square 0.05 m on a side. How many electrons are released per second, assuming every photon releases a photoelectron? How big a current would this be in amperes?

18.11 Roughly how many photons of visible light are given off per second by a 1-watt flashlight? (Only about 5 percent of the electric energy input to a tungsten-filament bulb is given off as visible light.)

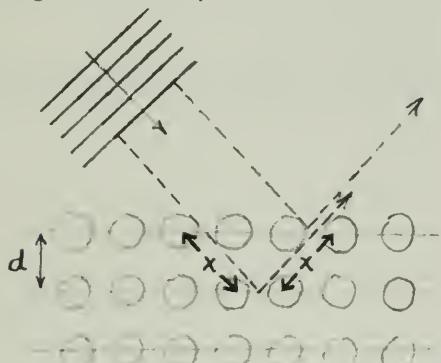
Hint: first find the energy, in joules, of an average photon of visible light.

18.12 Recall from Sec. 17.8 that 96,540 coulombs of charge will deposit 31.77 grams of copper in the electrolysis of copper sulfate. In Sec. 18.3, the charge of a single electron was reported to be 1.6×10^{-19} coulomb.

- How many electrons must be transferred to deposit 31.77 grams of copper?
- The density of copper is 8.92 grams per cm³. How many copper atoms would there be in the 1 cm³? (Actually copper has a combining number of 2, which suggests that 2 electrons are required to deposit a single copper atom.)
- What is the approximate volume of each copper atom?
- What is the approximate diameter of a copper atom? (For this rough approximation, assume that the atoms are cubes.)

*The MKSA unit for B is N/amp-m and is now called the *tesla*, (after the electrical engineer Nikola Tesla).

18.13 The approximate size of atoms can be calculated in a simple way from x-ray scattering experiments. The diagram below represents the paths of two portions of an x-ray wavefront, part of which is scattered from the first layer of atoms in a crystal, and part of which is scattered from the second layer. The part reflected from the second layer travels a distance $2x$ further before it emerges from the crystal.



- Under what conditions will the scattered wavefronts reinforce one another (that is, be in phase)?
- Under the conditions, will the scattered wavefronts cancel one another?
- Use trigonometry to express the relationship among wavelength λ , the distance d between layers, and the angle of reflection θ_{max} that will have maximum intensity.

18.14 The highest frequency, f_{max} , of the x rays produced by an x ray tube is given by the relation

$$hf_{max} = q_e V$$

where h is Planck's constant, q_e is the charge of an electron, and V is the potential difference at which the tube operates. If V is 50,000 volts, what is f_{max} ?

18.15 The equation giving the maximum energy of the x rays in the preceding problem looks like one of the equations in Einstein's theory of the photoelectric effect. How would you account for this similarity? For the difference?

18.16 What potential difference must be applied across an x-ray tube for it to emit x rays with a minimum wavelength of 10^{-11} m? What is the energy of these x rays in joules? In electron volts?

18.17 A *glossary* is a collection of terms limited to a special field of knowledge. Make a glossary of terms that appeared for the first time in this course in Chapter 18. Make an informative statement or definition for each term.

18.18 In his *Opticks*, Newton proposed a set of hypotheses about light which, taken together, constituted a fairly successful model of light. The hypotheses were stated as questions. Three of the hypotheses are given below:

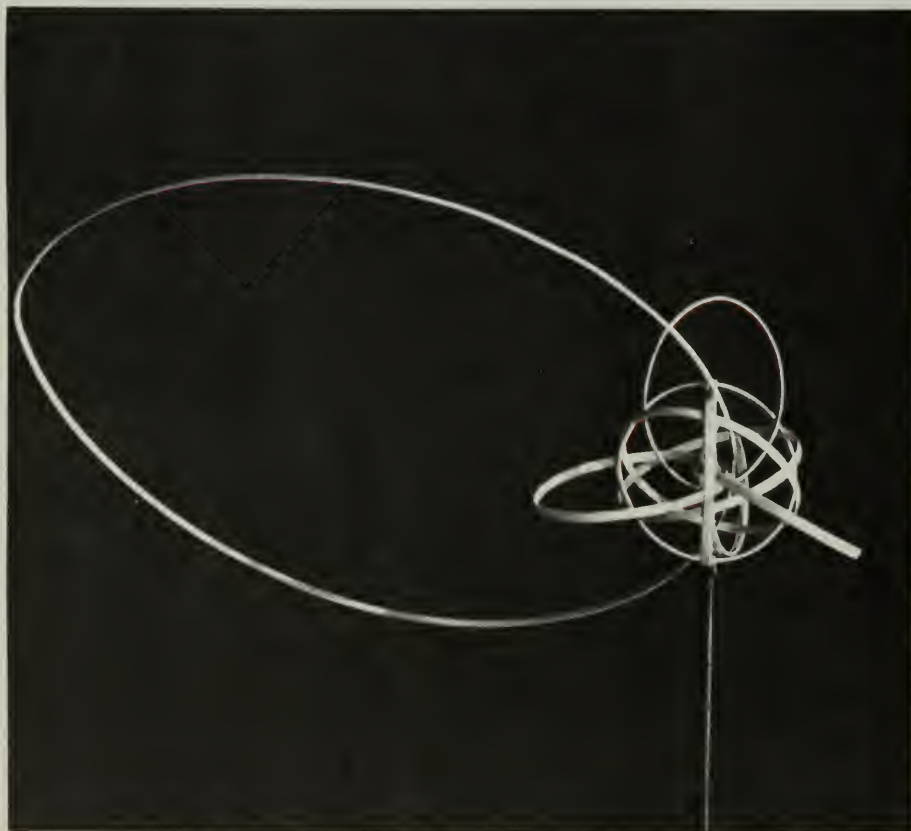
Are not all hypotheses erroneous, in which light is supposed to consist in pression or motion waves . . . ? [Quest. 28]

Are not the rays of light very small bodies emitted from shining substances? [Quest. 29]

Are not gross bodies and light convertible into one another, and may not bodies receive much of their activity from the particles of light which enter their composition? [Quest. 30]

- In what respect is Newton's model similar to and different from the photon model of light?
- Why would Newton's model be insufficient to explain the photoelectric effect? What predictions can we make with the photon model that we cannot with Newton's?

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Sculpture representing the Bohr model of a sodium atom.

CHAPTER NINETEEN

The Rutherford-Bohr Model of the Atom

19.1 Spectra of gases

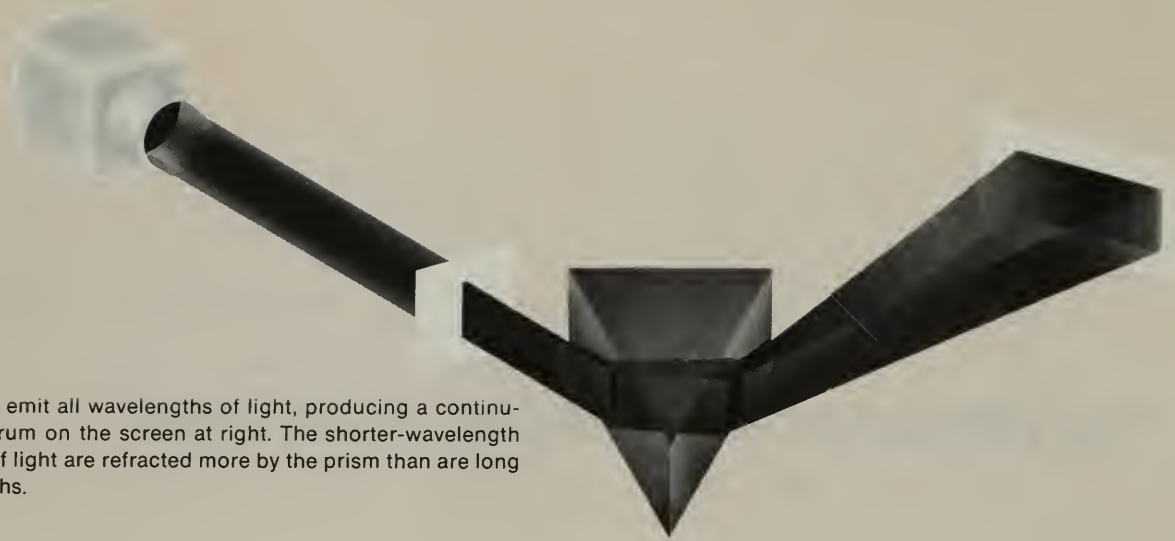
One of the first real clues to our understanding of atomic structure was provided by the study of the emission and absorption of light by samples of the elements. The results of this study are so important to our story that we shall review the history of their development in some detail.

SG 19.1

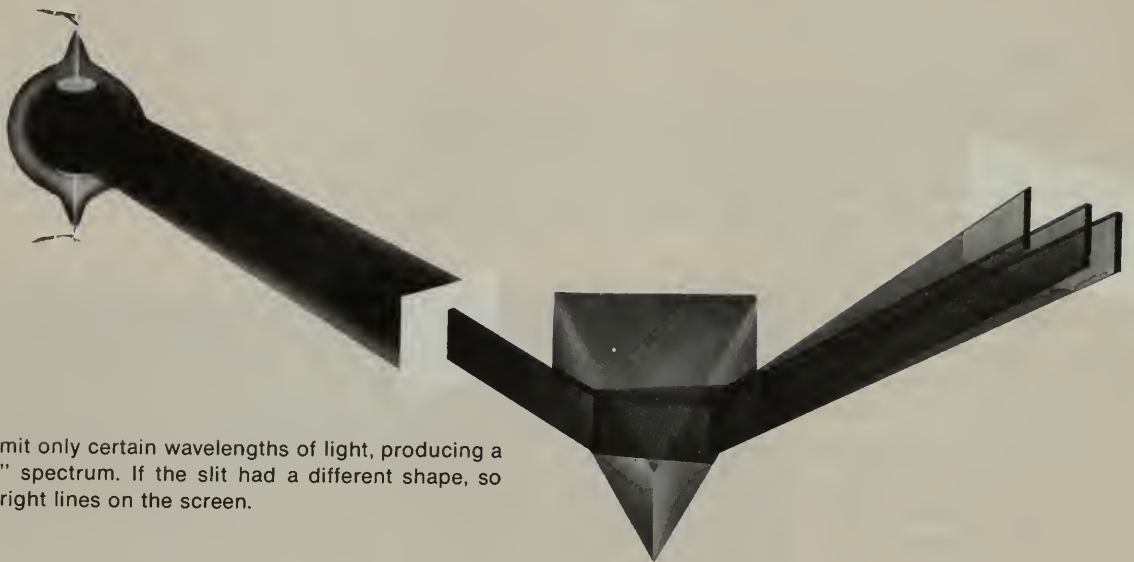
It had long been known that light is emitted by gases or vapors when they are excited in any one of several ways: by heating the gas to a high temperature, as when a volatile substance is put into a flame; by an electric discharge through gas in the space between the terminals of an electric arc; by a continuous electric current in a gas at low pressure (as in the now familiar “neon sign”).

The pioneer experiments on light emitted by various excited gases were made in 1752 by the Scottish physicist Thomas Melvill. He put one substance after another in a flame; and “having placed a pasteboard with a circular hole in it between my eye and the flame . . . , I examined the constitution of these different lights with a prism.” Melvill found the spectrum of light from a hot gas to be different from the well-known continuum of rainbow colors found in the spectrum of a glowing solid or liquid. Melvill’s spectrum consisted, not of an unbroken stretch of color continuously graded from violet to red, but of individual patches, each having the color of that part of the spectrum in which it was located, and with dark gaps (missing colors) between the patches. Later, when more general use was made of a narrow slit through which to pass the light, the emission spectrum of a gas was seen as a set of bright lines (see the figure in the margin on p. 61); the bright lines are in fact colored images of the slit. The existence of such spectra shows that light from a gas is a mixture of only a few definite colors or narrow wavelength regions of light.

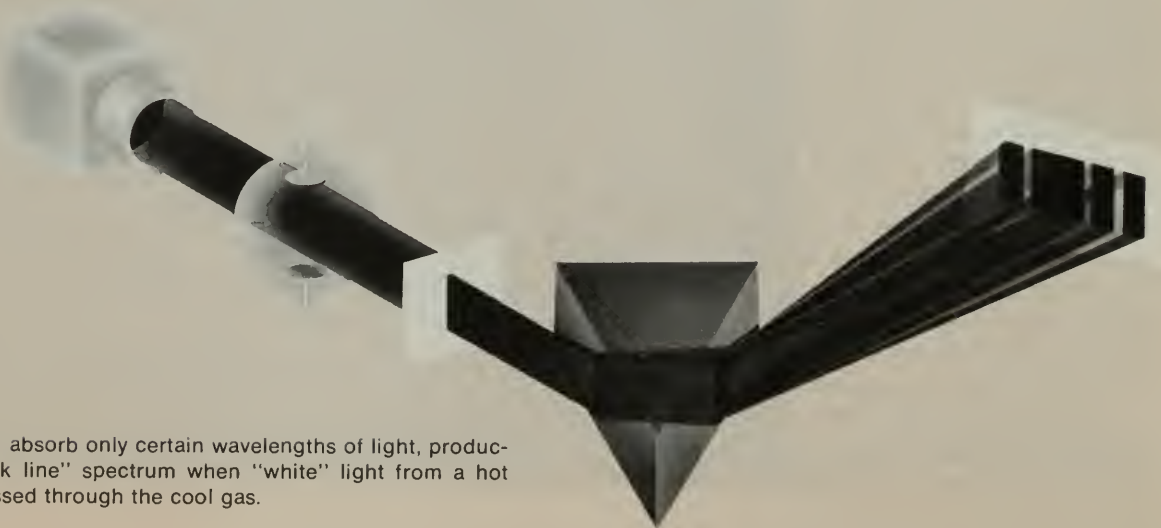
Melvill also noted that the colors and locations of the bright spots were different when different substances were put in the flame. For example, with ordinary table salt in the flame, the



Hot solids emit all wavelengths of light, producing a continuous spectrum on the screen at right. The shorter-wavelength portions of light are refracted more by the prism than are long wavelengths.



Hot gases emit only certain wavelengths of light, producing a "bright line" spectrum. If the slit had a different shape, so would the bright lines on the screen.



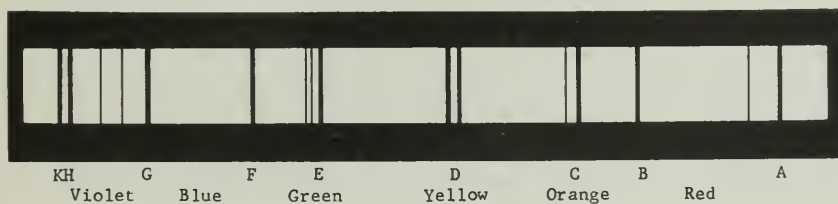
Cool gases absorb only certain wavelengths of light, producing a "dark line" spectrum when "white" light from a hot solid is passed through the cool gas.

predominant color was “bright yellow” (now known to be characteristic of the element sodium). In fact, the line emission spectrum is markedly different for each chemically different gas because each chemical element emits its own characteristic set of wavelengths (see the figure in the margin). In looking at a gaseous source without the aid of a prism or a grating, the eye combines the separate colors and perceives the mixture as reddish for glowing neon, pale blue for nitrogen, yellow for sodium vapor, and so on.

Some gases have relatively simple spectra. Thus the most prominent part of the visible spectrum of sodium vapor is a pair of bright yellow lines. Some gases or vapors have exceedingly complex spectra. Iron vapor, for example, has some 6000 bright lines in the visible range alone.

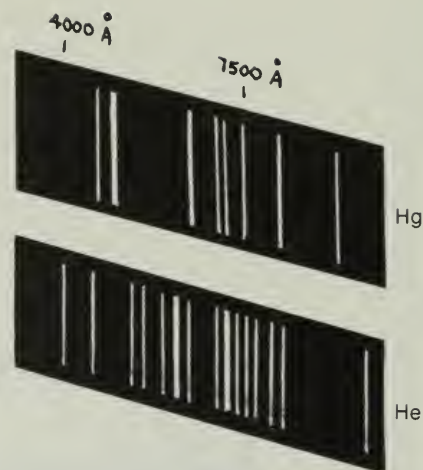
In 1823 the British astronomer John Herschel suggested that each gas could be identified from its unique line spectrum. By the early 1860's the physicist Gustave R. Kirchhoff and the chemist Robert W. Bunsen, in Germany, had jointly discovered two new elements (rubidium and cesium) by noting previously unreported emission lines in the spectrum of the vapor of a mineral water. This was the first of a series of such discoveries; it started the development of a technique making possible the speedy chemical analysis of small amounts of materials by *spectrum analysis*.

In 1802 the English scientist William Wollaston saw in the spectrum of sunlight something that had been overlooked before. Wollaston noticed a set of seven sharp, irregularly spaced *dark* lines across the continuous solar spectrum. He did not understand why they were there, and did not carry the investigation further. A dozen years later, the German physicist, Joseph von Fraunhofer, used better instruments and detected many hundreds of such dark lines. To the most prominent dark lines, Fraunhofer assigned the letters A, B, C, etc. These dark lines can be easily seen in the sun's spectrum with even quite simple modern spectroscopes, and his letters A, B, C . . . are still used to identify them.



In the spectra of several other bright stars, Fraunhofer found similar dark lines; many of them, although not all, were in the same positions as those in the solar spectrum.

The key observations toward a better understanding of both the dark-line and the bright-line spectra of gases were made by Kirchhoff in 1859. By that time it was known that the two prominent yellow lines in the emission spectrum of heated sodium vapor in the laboratory had the same wavelengths as two neighboring prominent dark lines in the solar spectrum to which Fraunhofer had



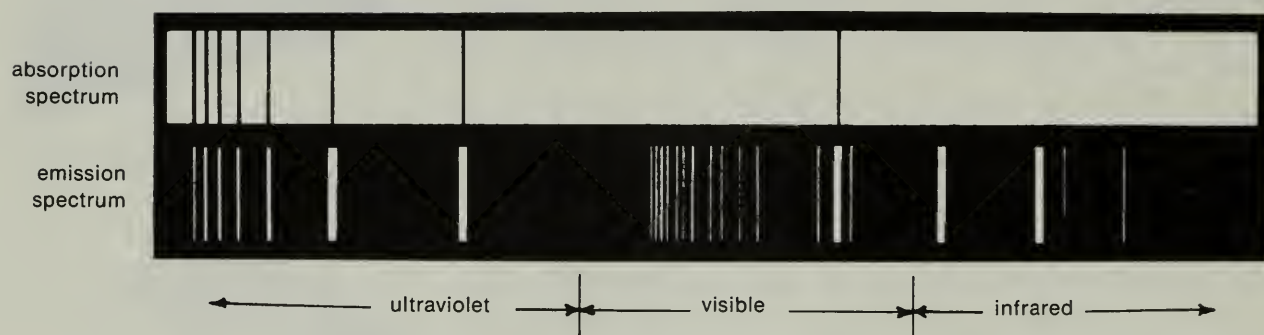
Parts of the line emission spectra of mercury (Hg) and helium (He), redrawn from photographic records.

Spectroscope: A device for examining the spectrum by eye.

Spectrometer or spectrograph: A device for measuring the wavelength of the spectrum and for recording the spectra (for example on film).

The Fraunhofer dark lines in the visible part of the solar spectrum; only a few of the most prominent lines are represented.

assigned the letter D. It was also known that the light emitted by a glowing solid forms a perfectly continuous spectrum that shows no dark lines. Kirchhoff now demonstrated that if the light from a glowing solid, as on page 60, is allowed first to pass through cooler sodium vapor and is then dispersed by a prism, the spectrum exhibits two prominent dark lines at the same place in the spectrum as the D-lines of the sun's spectrum. It was therefore reasonable to conclude that the light from the sun, too, was passing through a mass of sodium gas. This was the first evidence of the chemical composition of the gas envelope around the sun.



Comparison of the line absorption spectrum and line emission spectrum of sodium vapor.

When Kirchhoff's experiment was repeated with other relatively cool gases placed between a glowing solid and the prism, each gas was found to produce its own characteristic set of dark lines. Evidently each gas in some way absorbs light of certain wavelengths from the passing "white" light. More interesting still, Kirchhoff showed that the wavelength corresponding to each absorption line is equal to the wavelength of a bright line in the emission spectrum of the same gas. The conclusion is that a gas can absorb *only* light of these wavelengths which, when excited, it can emit. But note that not every emission line is represented in the absorption spectrum. (Soon you will see why.)

Each of the various Fraunhofer lines across the spectrum of the sun and also of far more distant stars have now been identified with the action of some gas as tested in the laboratory, and thereby the whole chemical composition of the outer region of the sun and other stars has been determined. This is really quite breathtaking from several points of view: (a) that it could be possible to find the chemical composition of immensely distant objects; (b) that the chemical materials there are the same as those in our own surroundings on earth, as shown by the fact that even the most complex absorption spectra are faithfully reproduced in the star spectra; and (c) that therefore the physical processes in the atom that are responsible for absorption must be the same here and there. In these facts we have a hint of how *universal* physical law really is: even at the outermost edges of the cosmos from which we get any light with absorbed wavelengths, the laws of physics appear to be the same as for common materials close at hand in our laboratory! This is just what Galileo and Newton had intuited when

they proposed that there is no difference between terrestrial and celestial physics.

Q1 What can you infer about the source if its light gives a bright line spectrum?

Q2 What can you infer about the source if its light gives a dark line spectrum?

Q3 What evidence is there that the physics and chemistry of materials at great distances from us is the same as of matter close at hand?

19.2 Regularities in the hydrogen spectrum

Of all the spectra, the line emission spectrum of hydrogen is especially interesting for both historical and theoretical reasons. In the visible and near ultraviolet regions, the emission spectrum consists of an apparently systematic series of lines whose positions are indicated at the right. In 1885, a Swiss school teacher, Johann Jakob Balmer, found a simple formula—an empirical relation—which gave the wavelengths of the lines known at the time. The formula is:

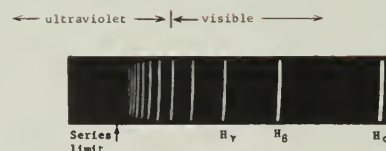
$$\lambda = b \left(\frac{n^2}{n^2 - 2^2} \right)$$

Where b is a constant which Balmer determined empirically and found to be equal to 3645.6 \AA , and n is a whole number, different for each line. Specifically, to give the observed value for the wavelength, n must be 3 for the first (red) line of the hydrogen emission spectrum (named H_α); $n = 4$ for the second (green) line (H_β); $n = 5$ for the third (blue) line (H_γ); and $n = 6$ for the fourth (violet) line (H_δ). The table below shows excellent agreement (within 0.02%) between the values Balmer computed from his empirical formula and previously measured values.

NAME OF LINE	n	Wavelength λ (in \AA)		
		FROM BALMER'S FORMULA	BY ANGSTROM'S MEASUREMENT	DIFFERENCE
H_α	3	6562.08	6562.10	+0.02
H_β	4	4860.8	4860.74	-0.06
H_γ	5	4340	4340.1	+0.1
H_δ	6	4101.3	4101.2	-0.1

It took nearly 30 years before anyone understood why Balmer's empirical formula worked so well—why the hydrogen atom emitted light whose wavelength made such a simple sequence. But this did not keep Balmer from speculating, that there might be other series of

Johann Jakob Balmer (1825-1898), a teacher at a girls' school in Switzerland, came to study wavelengths of spectra listed in tables through his interest in mathematical puzzles and numerology.



The Balmer lines of hydrogen; redrawn from a photograph made with a film sensitive to ultraviolet light as well as visible. The lines get more crowded as they approach the series limit in the ultraviolet.

Data on hydrogen spectrum (as given in Balmer's paper of 1885).

hitherto unsuspected lines in the hydrogen spectrum, and that their wavelengths could be found by replacing the 2^2 in the denominator of his equation by other numbers such as 1^2 , 3^2 , 4^2 , and so on. This suggestion, which stimulated many workers to search for such additional spectral series, turned out to be fruitful, as we shall discuss shortly.

To use modern notation, we first rewrite Balmer's formula in a form that will be more useful.

$$\frac{1}{\lambda} = R_H \left(\frac{1}{2^2} - \frac{1}{n^2} \right)$$

In this equation, which can be derived from the first one, R_H is a constant, equal to $4/b$. (It is called the *Rydberg constant for hydrogen*, in honor of the Swedish spectroscopist J. R. Rydberg who, following Balmer, made great progress in the search for various spectral series.) The series of lines described by Balmer's formula are called the Balmer series. While Balmer constructed his formula from known λ of only four lines, his formula predicted that there should be many more lines in the same series (indeed, infinitely many such lines as n takes on values such as $n = 3, 4, 5, 6, 7, 8, \dots \infty$). The figure in the margin indicates that this has indeed been observed—and every one of the lines is correctly predicted by Balmer's formula with considerable accuracy.

If we follow Balmer's speculative suggestion of replacing 2^2 by other numbers, we obtain the possibilities:

$$\frac{1}{\lambda} = R_H \left(\frac{1}{1^2} - \frac{1}{n^2} \right) \quad \frac{1}{\lambda} = R_H \left(\frac{1}{3^2} - \frac{1}{n^2} \right) \quad \frac{1}{\lambda} = R_H \left(\frac{1}{4^2} - \frac{1}{n^2} \right)$$

and so on. Each of these equations describes a possible series. All these hypothetical series of lines can then be summarized in one overall formula:

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

where n_f is a whole number that is fixed for any one series for which wavelengths are to be found (for example, it is 2 for all lines in the Balmer series). The letter n_i stands for integers that take on the values $n_f + 1, n_f + 2, n_f + 3, \dots$ for the successive individual lines in a given series (thus, for the first two lines of the Balmer series, n_i is 3 and 4.) The constant R_H should have the same value for all of these hydrogen series.

So far, our discussion has been merely speculation. No series, no single line fitting the formula in the general formula, need exist (—except for the observed Balmer series, where $n_f = 2$). But when physicists began to look for these hypothetical lines with good spectrometers—they found that they do exist!

In 1908, F. Paschen in Germany found two hydrogen lines in the infrared whose wavelengths were correctly given by setting $n_f = 3$ and $n_i = 4$ and 5 in the general formula; many other lines

H₁₀H₂₀

Part of the absorption spectrum of the star Rigel (β Orion). The dark lines are at the same location as lines due to absorption by hydrogen gas in the ultra-violet region; they match the lines of the Balmer series as indicated by the H numbers (where H₁ would be H _{α} , H₂ would be H _{β} etc.). This indicates the presence of hydrogen in the star.

in this “Paschen series” have since been identified. With improvements of experimental apparatus and techniques, new regions of the spectrum could be explored, and thus other series gradually were added to the Balmer and Paschen series. In the table below the name of each series listed is that of the discoverer.

Series of lines in the hydrogen spectrum

NAME OF SERIES	DATE OF DISCOVERY	REGION OF SPECTRUM	VALUES IN BALMER EQUATION
Lyman	1906-1914	ultraviolet	$n_f = 1, n_i = 2, 3, 4, \dots$
Balmer	1885	ultraviolet-visible	$n_f = 2, n_i = 3, 4, 5, \dots$
Paschen	1908	infrared	$n_f = 3, n_i = 4, 5, 6, \dots$
Brackett	1922	infrared	$n_f = 4, n_i = 5, 6, 7, \dots$
Pfund	1924	infrared	$n_f = 5, n_i = 6, 7, 8, \dots$

Balmer had also hoped that his formula for hydrogen spectra might be a pattern for finding series relationships in the observed spectra of other gases. This suggestion bore fruit also. While his formula itself did not work directly in describing spectra of gases other than hydrogen, it inspired formulas of similar mathematical form that were useful in expressing order in portions of a good many complex spectra. The Rydberg constant R_H also reappeared in such empirical formulas.

For three decades after Balmer’s success, physicists tried to account for spectra by constructing models of the atom that would radiate light of the right wavelengths. But the great number and variety of spectral lines, emitted even by the simplest atom, hydrogen, made it difficult to find a successful model. Eventually models were made that succeeded in revealing the origin of spectra and in this chapter and the next one, you will see how it was done.

What you have already learned in Chapter 18 about quantum theory suggests one line of attack: the emission and absorption of light from an atom must correspond to a decrease and an increase of the amount of energy the atom has. If atoms of an element emit light of only certain frequencies, then the energy of the atoms must be able to change only by certain amounts. These changes of energy must belong to some rearrangement of the parts of the atom.

SG 19.3-19.5

Q4 What evidence did Balmer have that there were other series of lines in the hydrogen spectrum, with terms $3^2, 4^2$, etc. instead of 2^2 ?

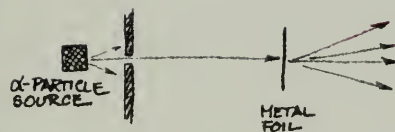
Q5 Often discoveries result from grand theories (like Newton’s) or from a good intuitive grasp of phenomena (like Faraday’s). What led Balmer to his relation for spectra?

Q6 What accounts for the success of Balmer’s overall formula in predicting new series of the emission spectrum of hydrogen?

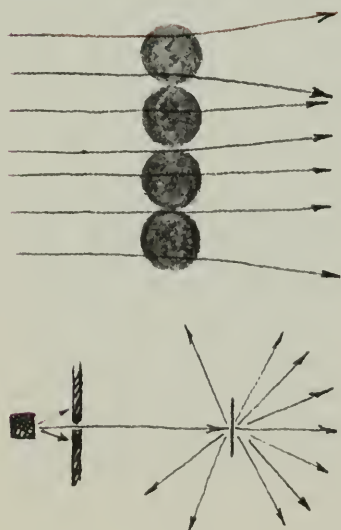
19.3 Rutherford's nuclear model of the atom

SG 19.6

A new basis for atomic models was provided during the period 1909 to 1911 by Ernest Rutherford, a New Zealander who had already shown ability as an experimentalist at McGill University in Montreal, Canada. He had been invited in 1907 to Manchester University in England where he headed a productive research laboratory. Rutherford was specially interested in the rays emitted by radioactive substances, in particular in α (alpha) rays. As we shall see in Chapter 21, α rays consist of positively charged particles. These particles are positively charged helium atoms with masses about 7500 times greater than the electron mass. Some radioactive substances emit α particles at rates and energies great enough for the particles to be used as projectiles to bombard samples of elements. The experiments that Rutherford and his colleagues did with α particles are examples of a highly important kind of experiment in atomic and nuclear physics—the scattering experiment.



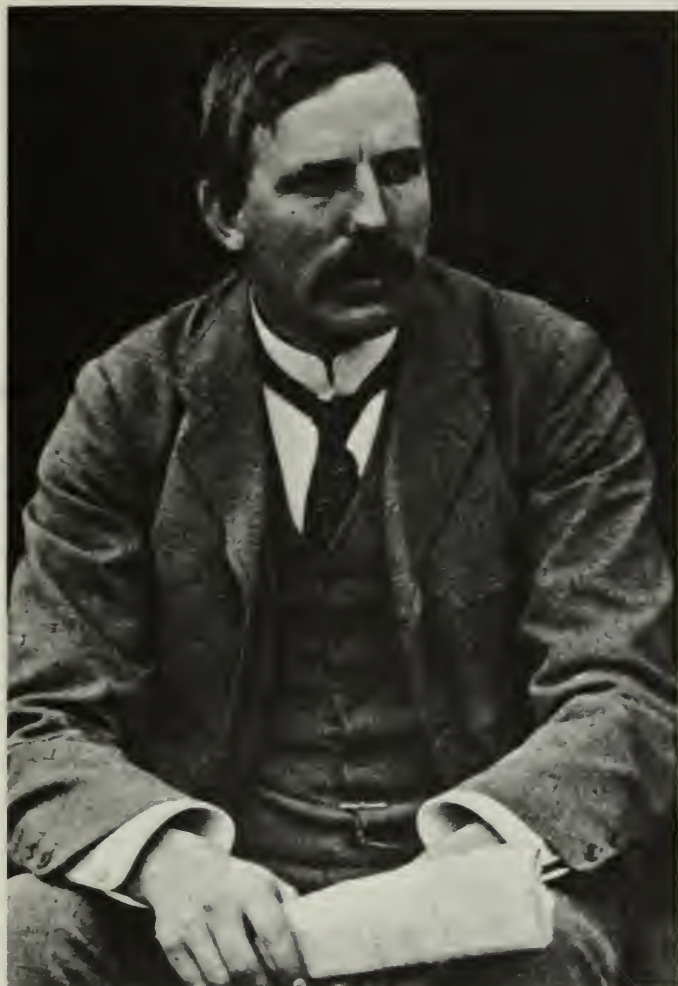
In somewhat the same way, you could, in principle, use a scattering experiment to discover the size and shape of an object hidden from view in a cloud or fog—by directing a series of projectiles at the unseen object and tracing their paths back after deflection.



In a scattering experiment, a narrow, parallel beam of projectiles (for example, α particles, electrons, x rays) is aimed at a target that is usually a thin foil or film of some material. As the beam strikes the target, some of the projectiles are deflected, or scattered from their original direction. The scattering is the result of the interaction between the particles in the beam and the atoms of the material. A careful study of the projectiles after they have been scattered can yield information about the projectiles, the atoms, or both—or the interaction between them. Thus if we know the mass, energy and direction of the projectiles, and see what happens to them in a scattering experiment, we can deduce properties of the atoms that scattered the projectiles.

Rutherford noticed that when a beam of α particles passed through a thin metal foil, the beam spread out. The scattering of α particles can be imagined to be caused by the electrostatic forces between the positively charged α particles and the charges that make up atoms. Since atoms contain both positive and negative charges, an α particle is subjected to both repulsive and attractive forces as it passes through matter. The magnitude and direction of these forces depend on how near the particle happens to approach to the centers of the atoms among which it moves. When a particular atomic model is proposed, the extent of the expected scattering can be calculated and compared with experiment. In the case of the Thomson model of the atom, calculation showed that the probability is so negligibly small that an α particle would be scattered through an angle of more than a few degrees.

The breakthrough to the modern model of the atom came when one of Rutherford's assistants, Hans Geiger, found that the number of particles scattered through angles of 10° or more was much greater than the number predicted on the basis of the Thomson model. In fact, one out of about every 8000 α particles was scattered through an angle greater than 90° . Thus a significant number of α particles virtually bounced right back from the foil. This result was entirely unexpected on the basis of Thomson's model of the atom,



Ernest Rutherford (1871-1937) was born, grew up, and received most of his education in New Zealand. At age 24 he went to Cambridge, England to work at the Cavendish Laboratory under J. J. Thomson. From there he went to McGill University in Canada, then home to be married and back to England again, now to Manchester University. At these universities, and later at the Cavendish Laboratory where he succeeded J. J. Thomson as director, Rutherford performed important experiments on radioactivity, the nuclear nature of the atom, and the structure of the nucleus. Rutherford introduced the concepts "alpha," "beta" and "gamma" rays, "protons," and "half-life." His contributions will be further discussed in Unit 6. For his scientific work, Rutherford was knighted and received a Nobel Prize.

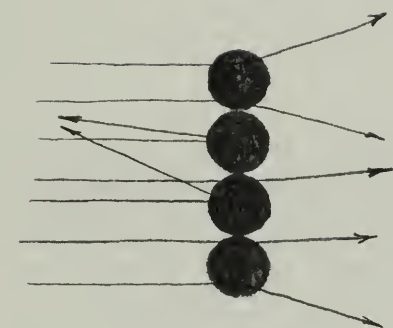
by which the atom should have acted on the projectile more like a cloud in which fine dust is suspended. Some years later, Rutherford wrote:

... I had observed the scattering of α -particles, and Dr. Geiger in my laboratory had examined it in detail. He found, in thin pieces of heavy metal, that the scattering was usually small, of the order of one degree. One day Geiger came to me and said, "Don't you think that young Marsden, whom I am training in radioactive methods, ought to begin a small research?" Now I had thought that, too, so I said, "Why not let him see if any α -particles can be scattered through a large angle?" I may tell you in confidence that I did not believe that they would be, since we knew that the α -particle was a very fast, massive particle, with a great deal of [kinetic] energy, and you could show that if the scattering was due to the accumulated effect of a number of small scatterings, the chance of an α -particle's being scattered backward was very small. Then I remember two or three days later Geiger coming to me in great excitement and saying, "We have

been able to get some of the α -particles coming backward . . ." It was quite the most incredible event that has ever happened to me in my life. It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you. On consideration, I realized that this scattering backward must be the result of a single collision, and when I made calculations I saw that it was impossible to get anything of that order of magnitude unless you took a system in which the greater part of the mass of the atom was concentrated in a minute nucleus. It was then that I had the idea of an atom with a minute massive centre, carrying a charge.

These experiments and Rutherford's interpretation marked the origin of the modern concept of the *nuclear atom*. Let us look at the experiments more closely to see why Rutherford concluded that the atom must have its mass and positive charge concentrated in a tiny space at the center, thus forming a nucleus about which the electrons are clustered.

A possible explanation of the observed scattering is that there exist in the foil concentrations of mass and charge—positively charged nuclei—much more dense than in Thomson's atoms. An α particle heading directly toward one of them is stopped and turned back, as a ball would bounce back from a rock but not from a cloud of dust particles. The figure in the margin is based on one of Rutherford's diagrams in his paper of 1911, which may be said to have laid the foundation for the modern theory of atomic structure. It shows two positively charged α particles, A and A'. The α particle A is heading directly toward a massive nucleus N. If the nucleus has a positive electric charge, it will repel the positive α particle. Because of the electrical repulsive force between the two, A is slowed to a stop at some distance r from N, and then moves directly back. A' is another α particle that is not headed directly toward the nucleus N; it is repelled by N along a path which calculation showed must be an hyperbola. The deflection of A' from its original path is indicated by the angle ϕ .



SG 19.6, 19.7



Paths of two α particles A and A' approaching a nucleus N. (Based on Rutherford, *Philosophical Magazine*, vol. 21 (1911), p. 669.)



Rutherford's scintillation apparatus was placed in an evacuated chamber so that the α particles would not be slowed down by collisions with air molecules.

Rutherford considered the effects on the path of the α particle due to the important variables—the α particle's speed, the foil thickness, and the quantity of charge Q on each nucleus. According to the model *most* of the α particles should be scattered through small angles, because the chance of approaching a very small nucleus nearly head-on is so small; but a noticeable number of α particles should be scattered through large angles.

Geiger and Marsden undertook tests of these predictions with the apparatus shown schematically in the margin. The lead box B contains a radioactive substance (radon) which emits α particles. The particles emerging from the small hole in the box are deflected through various angles ϕ in passing through the thin metal foil F. The number of particles deflected through each angle ϕ is found by letting the particles strike a zinc sulfide screen S. Each α particle that strikes the screen produces a scintillation (a momen-

tary pinpoint of fluorescence). These scintillations can be observed and counted by looking through the microscope M; S and M can be moved together along the arc of a circle. In later experiments, the number of α particles at any angle ϕ was counted more conveniently by replacing S and M by a counter invented by Geiger (see sketch in the margin). The Geiger counter, in its more recent versions, is now a standard laboratory item.

Geiger and Marsden found that the number of α particles counted depended on the scattering angle, the speed of the particles, and on the thickness of the foil of scattering material, just as Rutherford had predicted. This bore out the model of the atom in which most of the mass and all positive charge are concentrated in a very small region at the center of the atom.

Q7 Why are α particles scattered by atoms? Why is the angle of scattering mostly small but sometimes large?

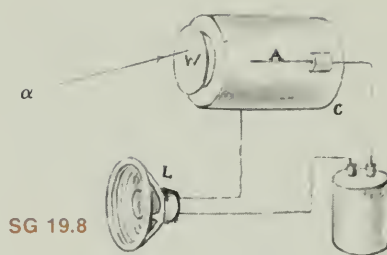
Q8 What was the basic difference between the Rutherford and the Thomson models of the atom?

19.4 Nuclear charge and size

At the time Rutherford made his predictions about the effect of the speed of the α particle and the thickness of foil on the angle of scattering, there was no way to measure independently the nucleus charge Q which he had to assume. However, some of Rutherford's predictions were confirmed by scattering experiments and, as often happens when part of a theory is confirmed, it is reasonable to proceed temporarily as if the whole of that theory were justified. That is, pending further proof, one could assume that the value of Q needed to explain the observed scattering data was the correct value of Q for the actual nucleus. On this basis, from the scattering by different elements—among them carbon, aluminum and gold—the following nuclear charges were obtained: for carbon, $Q = 6q_e$, for aluminum, $Q = 13$ or $14q_e$, and for gold, $Q = 78$ or $79q_e$. Similarly, tentative values were found for other elements.

The magnitude of the positive charge of the nucleus was an important and welcome piece of information about the atom. If the nucleus has a positive charge of $6q_e$, 13 to $14q_e$, etc., the number of electrons surrounding the nucleus must be 6 for carbon, 13 or 14 for aluminum, etc., since the atom as a whole is electrically neutral. This gave for the first time a good idea of just how many electrons an atom may have. But even more important, it was soon noticed that for each element the value found for the nuclear charge—in multiples of q_e —was close to the atomic number Z , the place number of that element in the periodic table! While the results of experiments on the scattering of α particles were not yet precise enough to permit this conclusion to be made with certainty, the data indicated that *each nucleus has a positive charge Q numerically equal to Zq_e .*

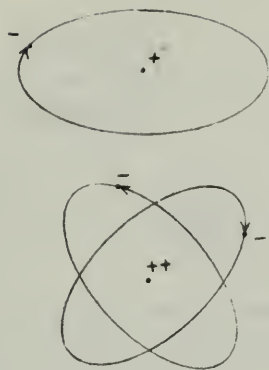
The suggestion that the number of positive charges on the



SG 19.8

A Geiger counter (1928). It consists of a metal cylinder C containing a gas and a thin axial wire A that is insulated from the cylinder. A potential difference slightly less than that needed to produce a discharge through the gas is maintained between the wire (anode A) and cylinder (cathode C). When an α particle enters through the thin mica window (W), it frees a few electrons from the gas molecules. The electrons are accelerated toward the anode, freeing more electrons along the way by collisions with gas molecules. The avalanche of electrons constitutes a sudden surge of current which may be amplified to produce a click in the loudspeaker (L) or to operate a register (as in the Project Physics scaler, used in experiments in Unit 6).

q = numerical value of charge of one electron.

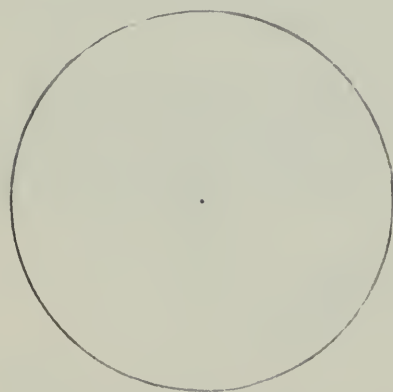


nucleus and also the number of electrons around the nucleus are equal to the atomic number Z made the picture of the nuclear atom at once much clearer and simpler. On this basis, the hydrogen atom ($Z = 1$) has one electron outside the nucleus; a helium atom ($Z = 2$) has in its neutral state two electrons outside the nucleus; a uranium atom ($Z = 92$) has 92 electrons. This simple scheme was made more plausible when additional experiments showed that it was possible to produce singly ionized hydrogen atoms, H^+ , and doubly ionized helium atoms, He^{++} , but not H^{++} or He^{+++} —evidently because a hydrogen atom has only one electron to lose, and a helium atom only two. Unexpectedly, the concept of the nuclear atom thus provided new insight into the periodic table of the elements: it suggested that the periodic table is really a listing of the elements according to *the number of electrons around the nucleus, or according to the number of positive units of charge on the nucleus*.

These results made it possible to understand some of the discrepancies in Mendeleev's periodic table. For example, the elements tellurium and iodine had been put into positions $Z = 52$ and $Z = 53$ on the basis of their chemical properties, contrary to the order of their atomic weights. Now that Z was seen to correspond to a fundamental fact about the nucleus, the reversed order of their atomic weights was understood to be a curious accident rather than a basic fault in the scheme.

As an important additional result of these scattering experiments the size of the nucleus may be estimated. Suppose an α particle is moving directly toward a nucleus. Its kinetic energy on approach is transformed into electrical potential energy. It slows down and eventually stops. The distance of closest approach may be computed from the original kinetic energy of the α particle and the charges of α particle and nucleus. (See SG 19.8.) The value calculated for the closest approach is approximately $3 \times 10^{-14}m$. If the α particle is not penetrating the nucleus, this distance must be at least as great as the sum of the radii of α particle and nucleus; so the radius of the nucleus could not be larger than about $10^{-14}m$, only about 1/1000 of the known radius of an atom. Thus if one considers its volume, which is proportional to the cube of the radius, it is clear that the atom is mostly empty, with the nucleus occupying only one billionth of the space! This in turn explains the ease with which α particles or electrons penetrate thousands of layers of atoms in metal foils or in gases, with only occasional large deflection backward.

Successful as this model of the nuclear atom was in explaining scattering phenomena, it raised many new questions: What is the arrangement of electrons about the nucleus? What keeps the negative electron from falling into a positive nucleus by electrical attraction? Of what is the nucleus composed? What keeps it from exploding on account of the repulsion of its positive charges? Rutherford openly realized the problems raised by these questions, and the failure of his model to answer them. But he rightly said that one should not expect one model, made on the basis of one



The central dot representing the nucleus in relation to the size of the atom as a whole is about 100 times too large. Popular diagrams of atoms often greatly exaggerate the relative size of the nucleus, (perhaps in order to suggest the greater mass).

set of puzzling results which it handled well, also to handle all other puzzles. Additional assumptions were needed to complete the model—to find answers to the additional questions posed about the details of atomic structure. The remainder of this chapter will deal with the theory proposed by Niels Bohr, a young Danish physicist who joined Rutherford's group just as the nuclear model was being announced.

SG 19.9

Q9 What does the “atomic number” of an element refer to, according to the Rutherford model of the atom?

Q10 What is the greatest positive charge that an ion of lithium (the next heaviest element after helium) could have?

19.5 The Bohr theory: the postulates

If an atom consists of a positively charged nucleus surrounded by a number of negatively charged electrons, what keeps the electrons from falling into the nucleus—from being pulled in by the electric force of attraction? One possible answer to this question is that an atom may be like a planetary system with the electrons revolving in orbits around the nucleus. Instead of the gravitational force, the electric attractive force between the nucleus and an electron would supply a centripetal force that would tend to keep the moving electron in orbit.

Although this idea seems to start us on the road to a theory of atomic structure, a serious problem arises concerning the stability of a planetary atom. According to Maxwell's theory of electromagnetism, a charged particle radiates energy when it is accelerated. Now, an electron moving in an orbit around a nucleus continually changes its velocity vector, always being accelerated by the centripetal electric force. The electron, therefore, should lose energy by emitting radiation. A detailed analysis of the motion of the electron shows that the electron should be drawn closer to the nucleus, somewhat as an artificial satellite that loses energy due to friction in the upper atmosphere spirals toward the earth. Within a very short time, the energy-radiating electron should actually be pulled into the nucleus. According to classical physics—mechanics and electromagnetism—a planetary atom would not be stable for more than a very small fraction of a second.

The idea of a planetary atom was nevertheless sufficiently appealing that physicists continued to look for a theory that would include a stable planetary structure and predict discrete line spectra for the elements. Niels Bohr, an unknown young Danish physicist who had just received his PhD degree, succeeded in constructing such a theory in 1912-1913. This theory, although it had to be modified later to make it applicable to many more phenomena, was widely recognized as a major victory, showing how to attack atomic problems by using quantum theory. In fact, even though it is now a comparatively naive way of thinking about the atom compared to the view given by more recent quantum-mechanical

Since Bohr incorporated Rutherford's idea of the nucleus, the model which Bohr's theory discusses is often called the Rutherford-Bohr model.



theories, Bohr's theory is a beautiful example of a successful physical model, measured by what it was designed to do.

Bohr introduced two novel postulates designed specifically to account for the existence of stable electron orbits and of the discrete emission spectra. These postulates may be stated as follows.

(1) Contrary to the expectations based on classical mechanics and electromagnetism, an atomic system can exist in any one of a number of states in which no emission of radiation takes place, even if the particles (electrons and nucleus) are in motion relative to each other. These states are called *stationary states* of the atom.

(2) Any emission or absorption of radiation, either as visible light or other electromagnetic radiation, will correspond to a sudden, discontinuous transition between two such stationary states. The radiation emitted or absorbed in a transition has a frequency f determined by the relation $hf = E_i - E_f$, where h is Planck's constant and E_i and E_f are the energies of the atom in the initial and final stationary states, respectively.

The quantum theory had begun with Planck's idea that *atoms emit light* only in definite amounts of energy; it was extended by Einstein's idea that *light travels* only as definite parcels of energy; and now it was extended further by Bohr's idea that *atoms exist* only in definite energy states. But Bohr also used the quantum concept in deciding *which* of all the conceivable stationary states of the atom were actually possible. An example of how Bohr did this is given in the next section.

For simplicity we consider the hydrogen atom, with a single electron revolving around the nucleus. Following Bohr, we assume that the possible electron orbits are simply circular. The details of some additional assumptions and the calculation are worked out on page 73. Bohr's result for the possible orbit radii r_n was $r_n = an^2$ where a is a constant ($h^2/4\pi^2mkq_e$) that can be calculated from known physical values, and n stands for any whole number, 1, 2, 3

Q11 What was the main evidence that an atom could exist only in certain energy states?

Q12 What reason did Bohr give for the atom existing only in certain energy states?

19.6 The size of the hydrogen atom

This is a remarkable result: in the hydrogen atom, the allowed orbital radii of the electrons are whole multiples of a constant that we can at once evaluate. That is n^2 takes on values of $1^2, 2^2, 3^2, \dots$, and all factors to the right of n^2 are quantities known previously by independent measurement! Calculating the value ($h^2/4\pi^2mkq_e$) gives us $5.3 \times 10^{-11}\text{m}$. Hence we now know that *according to Bohr's model* the radii of stable electron orbits should be $r_n = 5.3 \times 10^{-11}\text{m} \times n^2$. That is, $5.3 \times 10^{-11}\text{m}$ when $n = 1$ (first allowed orbit), $4 \times 5.3 = 21.2 \times 10^{-11}\text{m}$ when $n = 2$ (second allowed orbit), $9 \times 5.3 \times 10^{-11}\text{m}$ when $n = 3$, etc. In between these values, there are no allowed radii. In

Bohr's Quantization Rule and the Size of Orbits

The magnitude of the charge on the electron is q_e ; the charge on a nucleus is Zq_e , and for hydrogen ($Z = 1$) is just q_e . The electric force with which the hydrogen nucleus attracts its electron is therefore

$$F_{el} = k \frac{q_e q_e}{r^2}$$

where k is the coulomb constant, and r is the center-to-center distance. If the electron is in a stable circular orbit of radius r around the nucleus, moving at a constant speed v , then the centripetal force is equal to mv^2/r . Since the centripetal force is the electric attraction, we can write

$$\frac{mv^2}{r} = k \frac{q_e^2}{r^2}$$

In the last equation, m , q_e and k are constants; r and v are variables, whose values are related by the equation. What are the possible values of v and r for stationary states of the atom?

We can begin to get an answer if we write the last equation in slightly different form, by multiplying both sides by r^2 and dividing both sides by v ; the result is

$$mvr = \frac{kq_e^2}{v}$$

The quantity on the left side of this equation, which is the product of the momentum of the electron and the radius of the orbit, can be used to characterize the stable orbits. According to classical mechanics, the radius of the orbit could have any value, so the quantity mvr could also have any value. But we have seen that classical physics seemed to deny that there could be *any* stable orbits in the hydrogen atom. Since Bohr's first postulate implies that certain stable orbits (and only those) are permitted, Bohr needed to find the rule that decides *which* stable orbits were possible. Here Bohr appears to have been largely guided by his intuition. He found that what was needed was the recognition that the quantity mvr does not take on any arbitrary value, but only certain

discrete values. These values are defined by the relation

$$mvr = n \frac{h}{2\pi}$$

where h is Planck's constant, and n is a positive integer; that is, $n = 1, 2, 3, 4, \dots$ (but not zero). When the possible values of the mvr are restricted in this way, the quantity mvr is said to be *quantized*. The integer n which appears in the formula, is called the *quantum number*. The main point is that each quantum number ($n = 1$ or 2 or $3 \dots$) corresponds to one allowed, stable orbit of the electron.

If we accept this rule, we can at once describe the "allowed" states of the atom, say in terms of the radii r of the possible orbits. We can combine the last expression above with the classical centripetal force relation as follows: the quantization rule is

$$mvr = \frac{nh}{2\pi}$$

$$\text{so} \quad r = \frac{nh}{2\pi mv}$$

$$\text{and} \quad r^2 = \frac{n^2 h^2}{4\pi^2 m^2 v^2}$$

From classical mechanics, we had

$$\frac{mv^2}{r} = k \frac{q_e^2}{r^2}$$

$$\text{so} \quad v^2 = \frac{kq_e^2}{mr}$$

Substituting this "classical" value for v^2 into the quantization expression for r^2 gives

$$r^2 = \frac{n^2 h^2}{4\pi^2 m^2 \left(\frac{kq_e^2}{mr} \right)}$$

which simplifies to the expression for the allowed radii, r_n :

$$r_n = \frac{n^2 h^2}{4\pi^2 k m q_e^2}$$

SG 19.10

short, we have found that the separate allowed electron orbits are spaced around the nucleus in a regular way, with the allowed radii quantized in a regular manner, as indicated in the marginal drawing. Emission and absorption of light should then be accompanied by the transition of the electron from one allowed orbit to another.

This is just the kind of result we had hoped for; it tells us which radii are possible, and where they lie. But so far, it has all been model building. Do the orbits in a real hydrogen atom actually correspond to this model? In his first paper of 1913, Bohr could give at least a partial yes as answer: It was long known that the normal “unexcited” hydrogen atom has a radius of about 5×10^{-11} m. (That is, for example, the size of the atom obtained by interpreting measured characteristics of gases in the light of the kinetic theory.) This known value of 5×10^{-11} m corresponds excellently to the prediction from the equation for the orbital radius r if n has the lower value, namely 1. For the first time there was now a way to understand the size of the neutral, unexcited hydrogen atom: for every atom the size corresponds to the size of the innermost allowed electron orbit, and that is fixed by nature as described by the quantization rule.

Q13 Why do all unexcited hydrogen atoms have the same size?

Q14 Why does the hydrogen atom have just the size it has?

19.7 Other consequences of the Bohr model

With his two postulates and his choice of the permitted stationary states, Bohr could calculate not only the radius of each permitted orbit, but also the total energy of the electron in each orbit; this energy is the energy of the stationary state.

The results that Bohr obtained may be summarized in two simple formulas. As we saw, the radius of an orbit with quantum number n is given by the expression

$$r_n = n^2 r_1$$

where r_1 is the radius of the first orbit (the orbit for $n = 1$) and has the value 5.3×10^{-9} cm or 5.3×10^{-11} m.

The energy (including both kinetic and electric potential energy) of the electron in the orbit with quantum number n can be computed from Bohr's postulate also (see SG 19.11). As we pointed out in Chapter 10, it makes no sense to assign an absolute value to potential energy—since only *changes* in energy have physical meaning we can pick any convenient zero level. For an electron orbiting in an electric field, the mathematics is particularly simple if we choose as a zero level for energy the state $n = \infty$, that is, when the electron is infinitely far from the nucleus (and therefore free of it). If we consider the energy for any other state E_n to be

Note: Do not confuse this use of E for energy with earlier use of E for electric field.

the difference from this free state, we can write the possible energy states for the hydrogen atom as

$$E_n = \frac{1}{n^2} E_1$$

where E_1 is the total energy of the atom when the electron is in the first orbit; E_1 , the lowest energy possible for an electron in a hydrogen atom, is -13.6 eV (the negative value means only that the energy is 13.6 eV *less* than the free state value E_∞). This is called the “ground” state. In that state, the electron is most tightly “bound” to the nucleus. The value of E_2 , the first “excited” state above the ground state, is $1/2^2 \times -13.6$ eV $= -3.4$ eV, that is, only 3.4 eV less than in the free state.

According to the formula for r_n , the first Bohr orbit has the smallest radius, with $n = 1$. Higher values of n correspond to orbits that have larger radii. Although the higher orbits are spaced further and further apart, the force field of the nucleus falls off rapidly, so the work required to move out to the next larger orbit actually becomes smaller and smaller; therefore also the jumps in energy from one level of allowed energy E to the next become small and smaller.

19.8 The Bohr theory: the spectral series of hydrogen

It is commonly agreed that the most spectacular success of Bohr’s model was that it could be used to explain all emission (and absorption lines in the hydrogen spectrum. That is, Bohr could use his model to derive, and so to explain, the Balmer formula! By applying his second postulate, we know that the radiation emitted or absorbed in a transition in Bohr’s atom should have a frequency f determined by the relation

$$hf = E_i - E_f$$

If n_f is the quantum number of the final state, and n_i is the quantum number of the initial state, then according to the result for E_n we know that

$$E_f = \frac{1}{n_f^2} E_1 \quad \text{and} \quad E_i = \frac{1}{n_i^2} E_1$$

The frequency of radiation emitted or absorbed when the atom goes from the initial state to the final state is therefore determined by the equation

$$hf = \frac{E_1}{n_i^2} - \frac{E_1}{n_f^2} \quad \text{or} \quad hf = E_1 \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

To deal with wavelength λ (as in Balmer’s original formula, p. 63) rather than frequency f , we use now the relation between frequency and wavelength given in Unit 3: the frequency is equal to

See the radius and energy diagrams on page 78.



Niels Bohr (1885-1962) was born in Copenhagen, Denmark and was educated there, receiving his doctor's degree in physics in 1911. In 1912 he was at work in Rutherford's laboratory in Manchester, England, which was a center of research on radioactivity and atomic structure. There he developed his theory of atomic structure to explain chemical properties and atomic spectra. Bohr later played an important part in the development of quantum mechanics, in the advancement of nuclear physics, and in the study of the philosophical aspects of modern physics. In his later years he devoted much time to promoting plans for international cooperation and the peaceful uses of nuclear physics.



the speed of the light wave divided by its wavelength: $f = c/\lambda$. If we substitute c/λ for f in this equation, and then divide both sides by the constant hc (Planck's constant times the speed of light), we obtain the equation

$$\frac{1}{\lambda} = \frac{E_1}{hc} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

According to Bohr's model, then, this equation gives the wavelength λ of the radiation that will be emitted or absorbed when the state of a hydrogen atom changes from one stationary state with quantum number n_i to another with n_f .

How does this prediction from Bohr's model compare with the *empirical* Balmer formula for the Balmer series? The Balmer formula was given on page 64:

$$\frac{1}{\lambda} = R_H \left(\frac{1}{2^2} - \frac{1}{n^2} \right)$$

We see at once that the equation for λ of emitted (or absorbed) light derived from the Bohr model is exactly the same as Balmer's formula, if $R_H = -E_1/hc$ and $n_f = 2$.

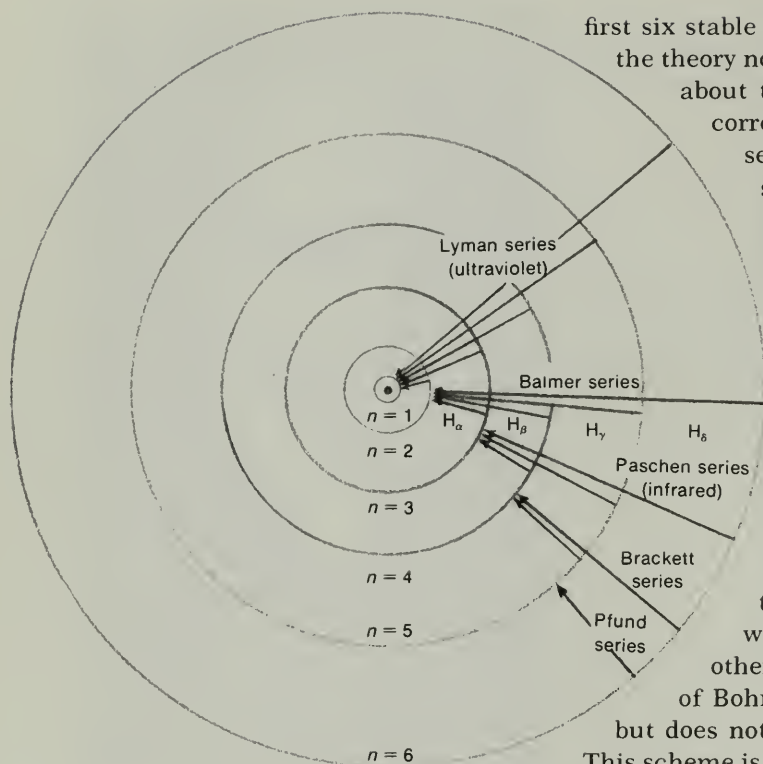
The Rydberg constant R_H , long known from spectroscopic measurements to have the value of $1.097 \times 10^7 \text{m}^{-1}$, now could be compared with the value for $-(E_1/hc)$. Remarkably, there was fine agreement. R_H , which had previously been regarded as just an experimentally determined constant, was now shown not to be arbitrary or accidental, but to depend on the mass and charge of the electron, on Planck's constant, and on the speed of light.

SG 19.11

More important, one now saw the *meaning*, in physical terms, of the old empirical formula for the Balmer series. All the lines in the Balmer series simply correspond to transitions from various initial states (various values of n_i) to the same final state, the state for which $n_f = 2$.

When the Bohr theory was proposed, in 1913, emission lines in only the Balmer and Paschen series for hydrogen were known definitely. Balmer had suggested, and the Bohr model agreed, that additional series should exist. The experimental search for these series yielded the discovery of the Lyman series in the ultraviolet portion of the spectrum (1916), the Brackett series (1922), and the Pfund series (1924). In each series the measured frequencies of the lines were found to be those predicted by Bohr's theory. Similarly, the general formula that Balmer guessed might apply for all spectral lines of hydrogen is explained; lines of the Lyman series correspond to transitions from various initial states to the final state $n_f = 1$, the lines of the Paschen series correspond to transitions from various initial states to the final state $n_f = 3$, etc. (see table on page 65). The general scheme of possible transitions among the

SG 19.12, 19.13



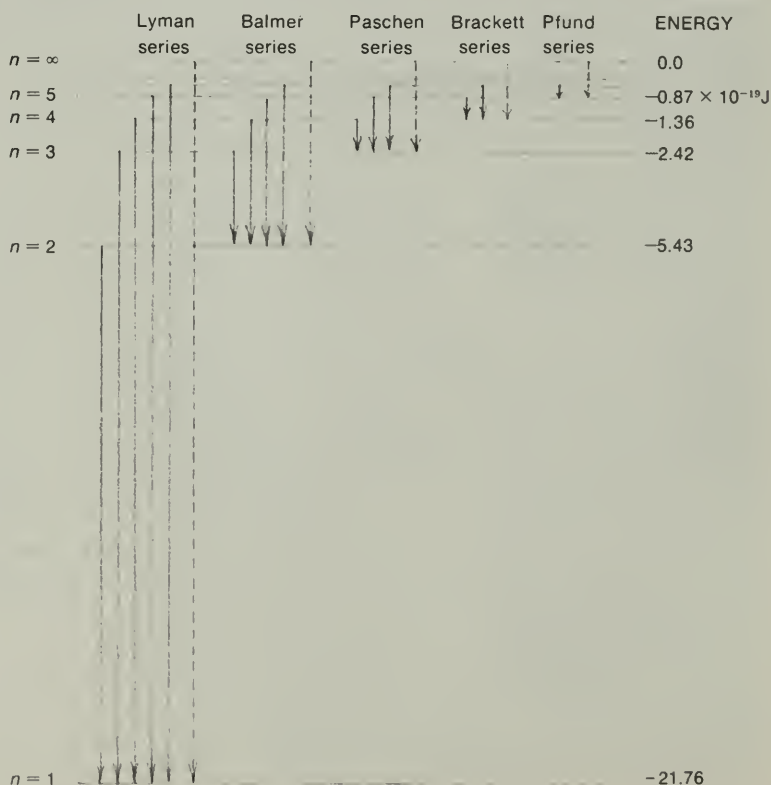
first six stable orbits is shown in the figure at the left. Thus the theory not only correlated currently known information about the spectrum of hydrogen, but also predicted correctly the wavelength of hitherto unknown series of lines in the spectrum. Moreover, it did so on a physically plausible model rather than, as Balmer's general formula had done, without any physical reason. All in all, these were indeed triumphs that are worth celebrating!

The schematic diagram shown at the left is useful as an aid for the imagination, but it also has the danger of being too specific. For instance, it leads us to visualize the emission of radiation in terms of "jumps" of electrons between orbits. These are useful ideas to aid our thinking, but one must not forget that we cannot actually detect an electron moving in an orbit, nor can we watch an electron "jump" from one orbit to another. Hence a second way of presenting the results of Bohr's theory is used which yields the same facts but does not commit us too closely to a picture of orbits.

This scheme is shown in the figure below. It focuses attention not on orbits but on the corresponding possible energy states, which

Above: A schematic diagram of the possible transitions of an electron in the Bohr model of the hydrogen atom (first six orbits).

At the right: Energy-level diagram for the hydrogen atom. Possible transitions between energy states are shown for the first six levels. The dotted arrow for each series indicates the *series limit*, a transition from the state where the electron is completely free (infinitely far) from the nucleus.



are all given by the formula $E_n = 1/n^2 \times E_1$. In terms of this *mathematical model*, the atom is normally unexcited, with an *energy* E_1 about -22×10^{-19} joules (-13.6 eV). Absorption of energy can place the atoms in an excited state, with a correspondingly higher energy. The excited atom is then ready to emit light, with a consequent reduction in energy. The energy absorbed or emitted always shifts the total energy of the atom to one of the values specified by the formula for E_n . We may thus, if we prefer, represent the hydrogen atom by means of the energy-level diagram.

Q15 Balmer had predicted accurately the other spectral series of hydrogen thirty years before Bohr did. Why is Bohr's prediction considered more significant?

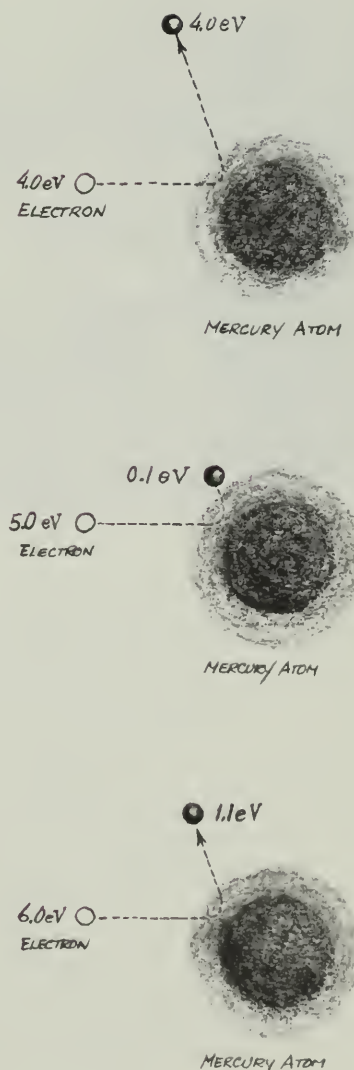
Q16 How does Bohr's model explain line absorption spectra?

19.9 Stationary states of atoms: the Franck-Hertz experiment

The success of the Bohr theory in accounting for the spectrum of hydrogen leaves this question: can experiments show directly that atoms have only certain discrete energy states? In other words, apart from the success of the idea in explaining spectra, are there really gaps between the energies that an atom can have? A famous experiment in 1914, by the German physicists James Franck and Gustav Hertz, showed the existence of these discrete energy states.

Franck and Hertz bombarded atoms with electrons (from an electron gun) and were able to measure the energy lost by electrons in collisions with atoms. They could also determine the energy gained by atoms in these collisions. In their first experiment, Franck and Hertz bombarded mercury vapor contained in a chamber at very low pressure. Their experimental procedure was equivalent to measuring the kinetic energy of electrons leaving the electron gun and the kinetic energy of electrons after they had passed through the mercury vapor. The only way electrons could lose energy was in collisions with mercury atoms. Franck and Hertz found that when the kinetic energy of the electrons leaving the electron gun was small, for example, up to several eV, the electrons after passage through the mercury vapor still had almost exactly the same energy as they had on leaving the gun. This result could be explained in the following way. A mercury atom is several hundred thousand times more massive than an electron. When it has low kinetic energy the electron just bounces off a mercury atom, much as a golf ball thrown at a bowling ball would bounce off. A collision of this kind is called an "elastic" collision. In an elastic collision, the mercury atom (bowling ball) takes up only an extremely small part of the kinetic energy of the electron (golf ball). The electron loses practically none of its kinetic energy.

But when the kinetic energy of the bombarding electrons was raised to 5 electron-volts, there was a dramatic change in the experimental results. When an electron collided with a mercury



The Nobel Prize



Alfred Bernhard Nobel (1833-1896), a Swedish chemist, was the inventor of dynamite. As a result of his studies of explosives, Nobel found that when nitroglycerine (an extremely unstable chemical) was absorbed in an inert substance it could be used safely as an explosive. This combination is dynamite. He also invented other explosives (blasting gelatin and ballistite) and detonators. Nobel was primarily interested in the peaceful uses of explosives, such as mining, road building and tunnel blasting, and he amassed a large fortune from the manufacture of explosives for these applications. Nobel abhorred war and was conscience-stricken by the military uses to which his explosives were put. At

his death, he left a fund of some \$315 million to honor important accomplishments in science, literature and international understanding. Prizes were established to be awarded each year to persons who have made notable contributions in the fields of physics, chemistry, medicine or physiology, literature or peace. (Since 1969 there has been a Nobel Memorial Prize in economics as well.) The first Nobel Prizes were awarded in 1901. Since then, men and women from about 30 countries have received prizes. At the award ceremonies the recipient receives a medal and the prize money from the king of Sweden, and is expected to deliver a lecture on his work. The Nobel Prize is generally considered the most prestigious prize in science.

Nobel Prize winners in Physics.

- 1901 Wilhelm Röntgen (Ger)—discovery of x-rays.
- 1902 H. A. Lorentz and P. Zeeman (Neth)—influence of magnetism on radiation.
- 1903 A. H. Becquerel (Fr)—discovery of spontaneous radioactivity. Pierre and Marie Curie (Fr)—work on rays first discovered by Becquerel.
- 1904 Lord Rayleigh (Gr Brit)—density of gases and discovery of argon.
- 1905 Philipp Lenard (Ger)—work on cathode rays.
- 1906 J. J. Thomson (Gr Brit)—conduction of electricity by gases.
- 1907 Albert A. Michelson (US)—optical precision instruments and spectroscopic and metrological investigations.
- 1908 Gabriel Lippmann (Fr)—color photography by interference.
- 1909 Guglielmo Marconi (Ital)—and Ferdinand Braum (Ger)—development of wireless telegraphy.
- 1910 Johannes van der Waals (Neth)—equation of state for gases and liquids.
- 1911 Wilhelm Wien (Ger)—laws governing the radiation of heat.
- 1912 Nils Gustaf Dalen (Swed)—automatic gas regulators for lighthouses and buoys.
- 1913 Kamerlingh Onnes (Neth)—low temperature and production of liquid helium.
- 1914 Max von Laue (Ger)—diffraction of Röntgen rays by crystals.
- 1915 W. H. and W. L. Bragg (Gr Brit)—analysis of crystal structure by Röntgen rays.
- 1916 No award.
- 1917 Charles Glover Barkla (Gr Brit)—discovery of Röntgen radiation of the elements.
- 1918 Max Planck (Ger)—discovery of energy quanta.
- 1919 Johannes Stark (Ger)—discovery of the Doppler effect in canal rays and the splitting of spectral lines in electric fields.
- 1920 Charles-Edouard Guillaume (Switz)—discovery of anomalies in nickel steel alloys.
- 1921 Albert Einstein (Ger)—for contributions to theoretical physics and especially for his discovery of the law of the photoelectric effect.
- 1922 Niels Bohr (Den)—atomic structure and radiation.
- 1923 Robert Andrews Millikan (US)—elementary charge of electricity and photoelectric effect.
- 1924 Karl Siegbahn (Swed)—field of x-ray spectroscopy.
- 1925 James Franck and Gustav Hertz (Ger)—laws governing the impact of an electron upon an atom.
- 1926 Jean Baptiste Perrin (Fr)—discontinuous structure of matter and especially for his discovery of sedimentation equilibrium.
- 1927 Arthur Compton (US)—discovery of effect named after him. C. T. R. Wilson (Gr Brit)—method of making paths of electrically charged particles visible by condensation of vapor.
- 1928 Owen Williams Richardson (Gr Brit)—thermionic phenomena and discovery of effect named after him.
- 1929 Louis-Victor de Broglie (Fr)—discovery of wave nature of electrons.
- 1930 Sir Chandrasekhara V. Raman (Ind)—scattering of light and effect named after him.
- 1931 No award.
- 1932 Werner Heisenberg (Ger)—quantum mechanics leading to discovery of allotropic forms of hydrogen.
- 1933 Erwin Schrödinger (Ger) and P. A. M. Dirac (Gr Brit)—new productive forms of atomic theory.
- 1934 No award.
- 1935 James Chadwick (Gr Brit)—discovery of the neutron.
- 1936 Victor Franz Hess (Aus.)—cosmic radiation. Carl David Anderson (US)—discovery of the positron.
- 1937 Clinton J. Davison (US)—and George P. Thomson (Gr Brit)—experimental diffraction of electrons by crystals.
- 1938 Enrico Fermi (Ital)—new radioactive elements produced by neutron irradiation and nuclear reactions by slow neutrons.
- 1939 Ernest O. Lawrence (US)—cyclotron and its use in regard to artificial radioactive elements.
- 1940 No award
- 1941 No award
- 1942 No award
- 1943 Otto Stern (Ger)—molecular ray method and magnetic moment of the proton.
- 1944 Isidor Isaac Rabi (US)—resonance method for magnetic properties of atomic nuclei.
- 1945 Wolfgang Pauli (Aus)—exclusion or Pauli principle.
- 1946 P. W. Bridgman (US)—high pressure physics.
- 1947 Sir Edward V. Appleton (Gr Brit)—physics of the upper atmosphere and discovery of so-called Appleton layers.
- 1948 Patrick M. S. Blackett, (Gr Brit)—development of Wilson cloud chamber and discoveries in nuclear physics and cosmic rays.
- 1949 Hideki Yukawa (Japan)—prediction of mesons and theory of nuclear forces.
- 1950 Cecil Frank Powell (Gr Brit)—Photographic method of studying nuclear processes and discoveries regarding mesons.
- 1951 Sir John D. Cockcroft and Ernest T. S. Walton (Gr Brit)—transmutation of atomic nuclei by artificially accelerated atomic particles.
- 1952 Felix Bloch (Switz) and Edward M. Purcell (US)—nuclear magnetic precision measurements.
- 1953 Frits Zernike (Neth)—phase-contrast microscope.
- 1954 Max Born (Ger)—statistical interpretation of wave functions, and Walter Bothe (Ger)—coincidence method for nuclear reactions and cosmic rays.
- 1955 Willis E. Lamb (US)—fine structure of hydrogen spectrum and Polykarp Kusch (US)—precision determinations of magnetic moment of electron.
- 1956 William Shockley, John Bardeen and Walter Houser Brattain (US)—researches on semiconductors and their discovery of the transistor effects.
- 1957 Chen Ning Yang and Tsung Dao Lee (Chin)—investigation of laws of parity, leading to discoveries regarding the elementary particles.
- 1958 Pavel A. Cerenkov, Il'ya M. Frank and Igor E. Tamm (USSR)—discovery and interpretation of the Cerenkov effect.
- 1959 Emilio G. Segre and Owen Chamberlain (US)—discovery of the antiproton.
- 1960 Donald A. Glaser (US)—invention of bubble chamber.
- 1961 Robert Hofstadter (US)—electron scattering in atomic nuclei. Rudolf Ludwig Mössbauer (Ger)—resonance absorption of γ -radiation and discovery of effect which bears his name.
- 1962 Lev D. Landau (USSR)—theories for condensed matter, especially liquid helium.
- 1963 Eugene P. Wigner (US)—theory of the atomic nucleus and elementary particles. Marie Goeppert-Mayer (US) and J. Hans D. Jensen (Ger)—nuclear shell structure.
- 1964 Charles Townes (US), Alexander Prokhorov and Nikolay Basov (USSR)—development of maser.
- 1965 S. Tomonaga (Japan), Julian Schwinger and Richard Feynman (US)—quantum electrodynamics and elementary particles.
- 1966 Alfred Kastler (Fr)—new optical methods for studying properties of atom.
- 1967 Hans Bethe (US)—nuclear physics and theory of energy production in the sun.
- 1968 Louis W. Alvarez (American) for research in physics of sub atomic particles and techniques for detection of these particles.
- 1969 Murray Gell-Mann (American) for contributions and discoveries concerning the classification of elementary particles and their interactions.

We now know two ways of “exciting” an atom: by absorption of a photon with just the right energy to make a transition from the lowest energy level to a higher one, or by doing the same thing by collision—with an electron from an electron gun, or by collision among agitated atoms (as in a heated enclosure or a discharge tube).

atom it lost almost exactly 4.9 eV of energy. And when the electron energy was increased to 6 eV, the electron still lost just 4.9 eV of energy in a collision with a mercury atom, being left with 1.1 eV of energy. These results indicated that a mercury atom cannot accept less than 4.9 eV of energy; and that when it is offered somewhat more, for example, 5 or 6 eV, it still can accept only 4.9 eV. The accepted amount of energy cannot go into kinetic energy of the mercury because of the relatively enormous mass of the atom as compared with that of an electron. Hence, Franck and Hertz concluded that the 4.9 eV of energy is added to the internal energy of the mercury atom—that the mercury atom has a stationary state with energy 4.9 eV greater than that of the lowest energy state, with no allowed energy level in between.

What happens to this extra 4.9 eV of internal energy? According to the Bohr model of atoms, this amount of energy should be emitted in the form of electromagnetic radiation when the atom returns to its lowest state. Franck and Hertz looked for this radiation, and found it. They observed that the mercury vapor emitted light at a wavelength of 2535 Å, a line known previously to exist in the emission spectrum of hot mercury vapor. The wavelength corresponds to a frequency f for which the photon's energy, hf , is just 4.9 eV (as you can calculate). This result showed that mercury atoms had indeed gained (and then radiated) 4.9 eV of energy in collisions with electrons.

SG 19.14, 19.15

Later experiments showed that mercury atoms bombarded by electrons could also gain other, sharply defined amounts of energy, for example, 6.7 eV and 10.4 eV. In each case radiation was emitted that corresponded to known lines in the emission spectrum of mercury; in each case analogous results were obtained. The electrons always lost energy, and the atoms always gained energy, both in sharply defined amounts. Each type of atom studied was found to have discrete energy states. The amounts of energy gained by the atoms in collisions with electrons could always be correlated with known spectrum lines. The existence of discrete or stationary states of atoms predicted by the Bohr theory of atomic spectra was thus verified by direct experiment. This verification was considered to provide strong confirmation of the validity of the Bohr theory.

SG 19.16

Q17 How much kinetic energy will an electron have after a collision with a mercury atom if its kinetic energy before collision is (a) 4.0 eV? (b) 5.0 eV? (c) 7.0 eV?

19.10 The periodic table of the elements

In the Rutherford-Bohr model, atoms of the different elements differ in the charge and mass of their nuclei, and in the number and arrangement of the electrons about each nucleus. Bohr came to picture the electronic orbits as shown on the next page, though not as a series of concentric rings in one plane but as tracing out

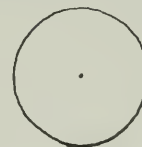
patterns in three dimensions. For example, the orbits of the two electrons of helium in the normal state are indicated as circles in planes inclined at about 60° with respect to each other. For each circular orbit, elliptical ones with the nucleus at one focus are also possible, and with the same (or nearly the same) total energy as in the circular orbit.

Bohr found a way of using his model to understand better the periodic table of the elements. In fact, it was the periodic table rather than the explanation of Balmer spectra that was Bohr's primary concern when he began his study. He suggested that the chemical and physical properties of an element depend on how the electrons are arranged around the nucleus. He also indicated how this might come about. He regarded the electrons in an atom as grouped together in layers or shells around the nucleus. Each shell can contain not more than a certain number of electrons. The chemical properties are related to how nearly full or empty a shell is. For example, full shells are associated with chemical stability, and in the inert gases the electron shells are completely filled.

To see how the Bohr model of atoms helps to understand chemical properties we may begin with the observation that the elements hydrogen ($Z = 1$) and lithium ($Z = 3$) are somewhat alike chemically. Both have valences of 1. Both enter into compounds of analogous types, for example hydrogen chloride, HCl , and lithium chloride, LiCl . Furthermore there are some similarities in their spectra. All this suggests that the lithium atom resembles the hydrogen atom in some important respects. Bohr conjectured that two of the three electrons of the lithium atom are relatively close to the nucleus, in orbits resembling those of the helium atom, while the third is in a circular or elliptical orbit outside the inner system. Since this inner system consists of a nucleus of charge $(+) 3q_e$ and two electrons each of the charge $(-) q_e$, its *net* charge is $(+) q_e$. Thus the lithium atom may be roughly pictured as having a central core of charge $(+) q_e$, around which one electron revolves, somewhat as for a hydrogen atom. The analogous physical structure, then, is the reason for the analogous chemical behavior.

Helium ($Z = 2$) is a chemically inert element, belonging to the family of noble gases. So far no one has been able to form compounds from it. These properties indicated that the helium atom is highly stable, having both of its electrons closely bound to the nucleus. It seemed sensible to regard both electrons as moving in the same *innermost shell* around the nucleus when the atom is unexcited. Moreover, because the helium atom is so stable and chemically inert, we may reasonably assume that this shell cannot accommodate more than two electrons. This shell is called the K-shell. The single electron of hydrogen is also said to be in the K-shell when the atom is unexcited. For lithium two electrons are in the K-shell, filling it to capacity, and the third electron starts a new one, called the L-shell. This single outlying and loosely bound electron is the reason for the strong chemical affinity of lithium for oxygen, chlorine, and many other elements.

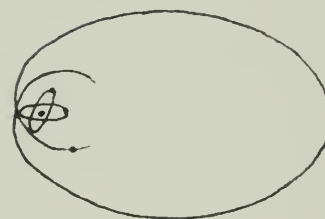
The sketches below are based on diagrams Bohr used in his university lectures.



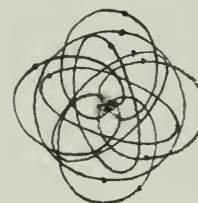
HYDROGEN ($Z=1$)



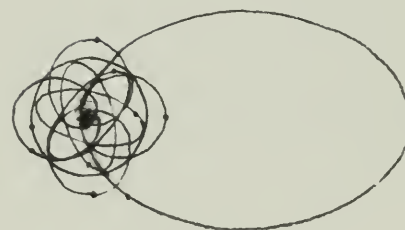
HELIUM ($Z=2$)



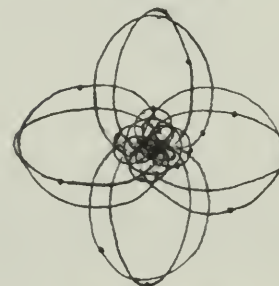
LITHIUM ($Z=3$)



NEON ($Z=10$)



SODIUM ($Z=11$)



ARGON ($Z=18$)

These two pages will be easier to follow if you refer to the table of the elements and the periodic table in Chapter 17 page 23.

Sodium ($Z = 11$) is the next element in the periodic table that has chemical properties similar to those of hydrogen and lithium, and this suggests that the sodium atom also is hydrogen-like in having a central core about which one electron revolves. Moreover, just as lithium follows helium in the periodic table, so does sodium follow another noble gas, neon ($Z = 10$). For the neon atom, we may assume that two of its 10 electrons are in the first (K) shell, and that the remaining 8 electrons are in the second (L) shell. Because of the chemical inertness and stability of neon, these 8 electrons may be expected to fill the L-shell to capacity. For sodium, then, the eleventh electron must be in a third shell, which is called the M-shell. Passing on to potassium ($Z = 19$), the next alkali metal in the periodic table, we again have the picture of an inner core and a single electron outside it. The core consists of a nucleus with charge (+) $19q_e$ and with 2, 8, and 8 electrons occupying the K-, L-, and M-shells, respectively. The 19th electron revolves around the core in a fourth shell, called the N-shell. The atom of the noble gas argon, with $Z = 18$, just before potassium in the periodic table, again represents a distribution of electrons in a tight and stable pattern, with 2 in the K-, 8 in the L-, and 8 in the M-shell.

These qualitative considerations have led us to a consistent picture of electrons distributed in groups, or shells, around the nucleus. The arrangement of electrons in the noble gases can be taken to be particularly stable, and each time we encounter a new alkali metal in Group I of the periodic table, a new shell is started; there is a single electron around a core which resembles the pattern for the preceding noble gas. We may expect that this outlying electron will easily come loose by the action of neighboring atoms, and this corresponds with the facts. The elements lithium, sodium and potassium belong to the group of alkali metals. In compounds or in solution (as in electrolysis) they may be considered to be in the form of ions such as Li^+ , Na^+ and K^+ , each lacking one electron and hence having one positive net charge (+) q_e . In the neutral atoms of these elements, the outer electron is relatively free to move about. This property has been used as the basis of a theory of electrical conductivity. According to this theory, a good conductor has many "free" electrons which can form a current under appropriate conditions. A poor conductor has relatively few "free" electrons. The alkali metals are all good conductors. Elements whose electron shells are filled are very poor conductors; they have no "free" electrons.

Shell name	Number of electrons in filled shell
K	2
L	8
M	18

Turning now to Group II of the periodic table, we would expect those elements that follow immediately after the alkali metals to have atoms with two outlying electrons. For example, beryllium ($Z = 4$) should have 2 electrons in the K-shell, thus filling it, and 2 in the L-shell. If the atoms of all these elements have two outlying electrons, they should be chemically similar, as indeed they are. Thus, calcium and magnesium, which belong to this group, should easily form ions such as Ca^{++} and Mg^{++} , each with a positive net charge of (+) $2q_e$, and this is also found to be true.

As a final example, consider those elements that immediately *precede* the noble gases in the periodic table. For example, fluorine atoms ($Z = 9$) should have 2 electrons filling the K-shell but only 7 electrons in the L-shell, which is one less than enough to fill it. If a fluorine atom should capture an additional electron, it should become an ion F^- with one negative net charge. The L-shell would then be filled, as it is for neutral neon ($Z = 10$), and thus we would expect the F^- ion to be relatively stable. This prediction is in accord with observation. Indeed, all the elements immediately preceding the inert gases in the periodic table tend to form stable singly-charged negative ions in solution. In the solid state, we would expect these elements to be lacking in free electrons, and all of them are in fact poor conductors of electricity.

Altogether there are seven main shells, K, L, M, . . . Q, and further analysis shows that all but the first are divided into *subshells*. The second (L) shell consists of two subshells, the third (M) shell consists of three subshells, and so on. The first subshell in any shell can always hold up to 2 electrons, the second up to 6, the third up to 10, the fourth up to 14, and so on. For all the elements up to and including argon ($Z = 18$), the buildup of electrons proceeds quite simply. Thus the argon atom has 2 electrons in the K-shell, 8 in the L-shell, then 2 in the first M-subshell and 6 in the second M-subshell. But the first subshell of the N-shell is lower in energy than the third subshell of the M-shell. Since atoms are most likely to be in the lowest energy state available, the N-shell will begin to fill before the M-shell is completed. Therefore, after argon, there may be electrons in an outer shell before an inner one is filled.



SG 19.17, 19.18

Relative energy levels of electron states in atoms. Each circle represents a state which can be occupied by 2 electrons.

This complicates the scheme somewhat but still allows it to be consistent. The arrangement of the electrons in any unexcited atom is always the one that provides greatest stability for the whole atom. And according to this model, chemical phenomena generally involve only the outermost electrons of the atoms.

Bohr carried through a complete analysis along these lines and, in 1921, proposed the form of the periodic table shown below. The periodicity results from the completion of subshells, which is complicated even beyond the shell overlap in the figure on page 85 by the interaction of electrons in the same subshell. This still useful table was the result of *physical* theory and offered a fundamental *physical* basis for understanding chemistry—for example, how the structure of the periodic table follows from the shell structure of atoms. This was another triumph of the Bohr theory.

Period	Period I	Period II	Period III	Period IV	Period V	Period VI	Period VII
I	1 H						
II	2 He	3 Li, 4 Be, 5 B, 6 C, 7 N, 8 O, 9 F, 10 Ne	11 Na, 12 Mg, 13 Al, 14 Si, 15 P, 16 S, 17 Cl, 18 Ar	19 K, 20 Ca, 21 Sc, 22 Ti, 23 V, 24 Cr, 25 Mn, 26 Fe, 27 Co, 28 Ni, 29 Cu, 30 Zn, 31 Ga, 32 Ge, 33 As, 34 Se, 35 Br, 36 Kr	37 Rb, 38 Sr, 39 Y, 40 Zr, 41 Nb, 42 Mo, 43 Ma, 44 Ru, 45 Rh, 46 Pd, 47 Ag, 48 Cd, 49 In, 50 Sn, 51 Sb, 52 Te, 53 I, 54 Xe	55 Cs, 56 Ba, 57 La, 58 Ce, 59 Pr, 60 Nd, 61 Il, 62 Sa, 63 Eu, 64 Gd, 65 Tb, 66 Dy, 67 Ho, 68 Er, 69 Tu, 70 Yb, 71 Lu, 72 Hf, 73 Ta, 74 W, 75 Re, 76 Os, 77 Ir, 78 Pt, 79 Au, 80 Hg, 81 Tl, 82 Pb, 83 Bi, 84 Po, 85 --, 86 Nt	87 --, 88 Ra, 89 Ac, 90 Th, 91 Pa, 92 U

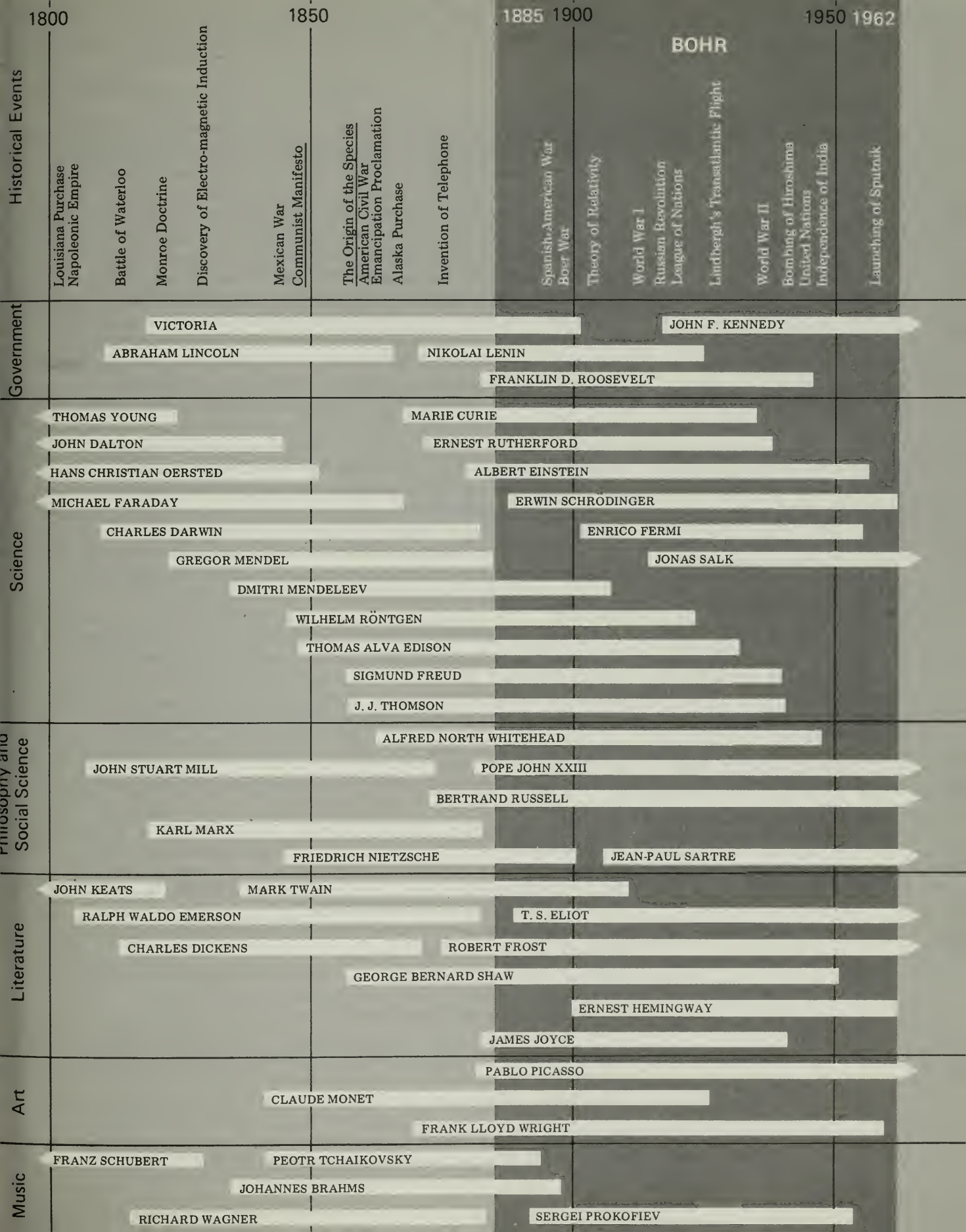
Bohr's periodic table of the elements (1921). For example some of the names and symbols have been changed. Masurium (43) is now called Technetium (43), and Niton (86) is Radon (86). The rectangles indicate the filling of subshells of a higher shell.

Q18 Why do the next heavier elements after the noble gases easily become positively charged?

Q19 Why are there only 2 elements in Period I, 8 in Period II, 8 in Period III, etc?

19.11 The inadequacy of the Bohr theory, and the state of atomic theory in the early 1920's

As we are quite prepared to find, every model, every theory has limits. In spite of the successes achieved with the Bohr theory in the years between 1913 and 1924, problems arose for which the



In March 1913, Bohr wrote to Rutherford enclosing a draft of his first paper on the quantum theory of atomic constitution. On March 20, 1913, Rutherford replied in a letter, the first part of which we quote, "Dear Dr. Bohr:

I have received your paper and read it with great interest, but I want to look it over again carefully when I have more leisure. Your ideas as to the mode of origin of spectra in hydrogen are very ingenious and seem to work out well; but the mixture of Planck's ideas with the old mechanics makes it very difficult to form a physical idea of what is the basis of it. There appears to me one grave difficulty in your hypothesis, which I have no doubt you fully realize, namely, how does an electron decide what frequency it is going to vibrate at when it passes from one stationary state to the other. It seems to me that you would have to assume that the electron knows before hand where it is going to stop. . . .

theory proved inadequate. Bohr's theory accounted excellently for the spectra of atoms with a single electron in the outermost shell, but serious discrepancies between theory and experiment appeared in the spectra of atoms with two electrons or more in the outermost shell. It was also found experimentally that when a sample of an element is placed in an electric or magnetic field, its emission spectrum shows additional lines. For example, in a magnetic field each line is split into several lines. The Bohr theory could not account in a quantitative way for the observed splitting. Further, the theory supplied no method for predicting the relative brightness of spectral lines. These relative intensities depend on the probabilities with which atoms in a sample undergo transitions among the stationary states. Physicists wanted to be able to calculate the probability of a transition from one stationary state to another. They could not make such calculations with the Bohr theory.

By the early 1920's it had become clear that the Bohr theory, despite its great successes, was deficient beyond certain limits. It was understood that to get a theory that would be successful in solving more problems, Bohr's theory would have to be revised, or replaced by a new one. But the successes of Bohr's theory showed that a better theory of atomic structure would still have to account also for the existence of stationary states—discrete atomic energy levels—and would, therefore, have to be based on quantum concepts.

Besides the inability to predict certain properties of atoms at all, the Bohr theory had two additional shortcomings: it predicted some results that were not in accord with experiment (such as the spectra of elements with two or three electrons in the outermost electron shells); and it predicted others that could not be tested in any known way (such as the details of electron orbits). Although orbits were easy to draw on paper, they could not be observed directly, nor could they be related to any observable properties of atoms. Planetary theory has very different implications when applied to a real planet moving in an orbit around the sun, and when applied to an electron in an atom. The precise position of a planet is important, especially if we want to do experiments such as photographing an eclipse, or a portion of the surface of Mars from a satellite. But the moment-to-moment position of an electron in an orbit has no such meaning because it has no relation to any experiment physicists have been able to devise. It thus became evident that, in using the Bohr theory, physicists could be led to ask some questions which could not be answered experimentally.

In the early 1920's, physicists—above all, Bohr himself—began to work seriously on the revision of the basic ideas of the theory. One fact that stood out was that the theory started with a *mixture* of classical and quantum ideas. An atom was assumed to act in accordance with the laws of classical physics up to the point where these laws did not work; then the quantum ideas were introduced. The picture of the atom that emerged from this inconsistent mixture was a combination of ideas from classical physics and concepts for

which there was no place in classical physics. The orbits of the electrons were determined by the classical, Newtonian laws of motion. But of the many possible orbits, only a small portion were regarded as possible, and these were selected by rules that contradicted classical mechanics. Or again, the frequency calculated for the orbital revolution of electrons was quite different from the frequency of light emitted or absorbed when the electron moved from or to this orbit. Or again, the decision that n could never be zero was purely arbitrary, just to prevent the model from collapsing by letting the electron fall on the nucleus. It became evident that a better theory of atomic structure would have to be built on a more consistent foundation in quantum concepts.

In retrospect, the contribution of the Bohr theory may be summarized as follows. It provided some excellent answers to earlier questions raised about atomic structure in Chapters 17 and 18. Although the theory turned out to be inadequate it drew attention to how quantum concepts can be used. It indicated the path that a new theory would have to take. A new theory would have to supply the right answers that the Bohr theory gave, and would also have to supply the right answers for the problems the Bohr theory could not solve. And without doubt one of the most intriguing aspects of Bohr's work was the proof that physical and chemical properties of matter can be traced back to the fundamental role of *integers* – (quantum numbers such as $n = 1, 2, 3 \dots$). As Bohr said, “The solution of one of the boldest dreams of natural science is to build up an understanding of the regularities of nature upon the consideration of pure number.” We catch here an echo of the hope of Pythagoras and Plato, of Kepler and Galileo.

Since the 1920's, a successful theory of atomic structure has been developed and has been generally accepted by physicists. It is part of “quantum mechanics,” so called because it is built directly on quantum concepts; it goes now far beyond understanding atomic structure, and in fact is the basis of our modern conception of events on a submicroscopic scale. Some aspects will be discussed in the next chapter. Significantly, Bohr himself was again a leading contributor.

Remember, for example, (in Unit 1) how proudly Galileo pointed out, when announcing that all falling bodies are equally and constantly accelerated: “So far as I know, no one has yet pointed out that the distances traversed, during equal intervals of time, by a body falling from rest, stand to one another in the same ratio as the odd numbers beginning with unity [namely 1:3:5:7: . . .].”

SG 19.19–19.23

Q20 The Bohr model of atoms is widely given in science books. What is wrong with it? What is good about it?

19.1 The Project Physics materials particularly appropriate for Chapter 19 include:

Experiment

Spectroscopy

Activities

Scientists on stamps
Measuring ionization, a quantum effect
"Black box" atoms

Reader Article

The Teacher and the Bohr Theory of the Atom

Film Loop

Rutherford Scattering

Transparencies

Alpha Scattering
Energy Levels—Bohr Theory

- 19.2** (a) Suggest experiments to show which of the Fraunhofer lines in the spectrum of sunlight are due to absorption in the sun's atmosphere rather than to absorption by gases in the earth's atmosphere.
- (b) How might one decide from spectroscopic observations whether the moon and the planets shine by their own light or by reflected light from the sun?

19.3 Theoretically, how many series of lines are there in the emission spectrum of hydrogen? In all these series, how many lines are in the visible region?

19.4 The Rydberg constant for hydrogen, R_H , has the value $1.097 \times 10^7/\text{m}$. Calculate the wavelengths of the lines in the Balmer series corresponding to $n = 8$, $n = 10$, $n = 12$. Compare the values you get with the wavelengths listed in the table on p. 63. Do you see any trend in the values?

- 19.5** (a) As indicated in the figure on p. 63 the lines in one of hydrogen's spectral series are bunched very closely at one end. Does the formula

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

suggest that such bunching will occur?

- (b) The "series limit" corresponds to the last possible line(s) of the series. What value should be taken for n_i in the above equation to compute the wavelength of the series limit?
- (c) Compute the series limit for the Lyman, Balmer, or Paschen series of hydrogen.
- (d) Consider a photon with a wavelength corresponding to the series limit of the Lyman series. What energy could it carry? Express the answer in joules and in electron volts ($1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$).

19.6 In what ways do Thomson's and Rutherford's atomic models agree? In what ways do they disagree?

19.7 In 1903, the German physicist Philipp Lenard (1864-1947) proposed an atomic model different from those of Thomson and Rutherford. He observed that, since cathode-ray particles can penetrate matter, most of the atomic volume must offer no obstacle to their penetration. In Lenard's model there were no electrons and no positive charges separate from the electrons. His atom was made up of particles called *dynamides*, each of which was an electric doublet possessing mass. (An electric doublet is a combination of a positive charge and a negative charge very close together.) All the dynamides were supposed to be identical, and an atom contained as many of them as were needed to make up its mass. They were distributed throughout the volume of the atom, but their radius was so small compared with that of the atom that most of the atom was empty.

- (a) In what ways does Lenard's model agree with those of Thomson and Rutherford? In what ways does it disagree with those models?
- (b) Why would you not expect α particles to be scattered through large angles if Lenard's model were valid?
- (c) In view of the scattering of α particles that is observed, is Lenard's model valid?

19.8 Determine a plausible upper limit for the effective size of a gold atom from the following facts and hypotheses:

- i. A beam of α -particles of known velocity $v = 2 \times 10^7 \text{ m/sec}$ is scattered from a gold foil in a manner explicable only if the α particles were repelled by nuclear charges that exert a Coulomb's law repulsion on the α particles.
- ii. Some of these α particles come straight back after scattering. They therefore approached the nuclei up to a distance r from the nucleus' center, where the initial kinetic energy $\frac{1}{2} m_\alpha v_\alpha^2$ has been completely changed to the potential energy of the system.
- iii. The potential energy of a system made up of an α particle of charge $2q_e$ at a distance r from a nucleus of charge Zq_e is given by the product of the "potential" (Zq_e/r) set up by the nucleus at distance r , and the charge ($2q_e$) of the α particle.
- iv. The distance r can now be computed, since we know v_α , m_α ($7 \times 10^{-27} \text{ kg}$, from other evidences to be discussed in Unit 6), Z for gold atoms (see periodic table), q_e (see Section 14.5).
- v. The nuclear radius must be equal to or less than r . Thus we have a plausible upper limit for the size of this nucleus.

19.9 We generally suppose that the atom and the nucleus are each spherical, that the diameter of the atom is of the order of 1 \AA (Ångstrom unit = 10^{-10} m) and that the diameter of the nucleus is of the order of 10^{-12} cm .

- What are the evidences that these are reasonable suppositions?
- What is the ratio of the diameter of the nucleus to that of the atom?

19.10 The nucleus of the hydrogen atom is thought to have a radius of about $1.5 \times 10^{-13} \text{ cm}$. If the atom were magnified so that the nucleus is 0.1 mm across (the size of a grain of dust), how far away from it would the electron be in the Bohr orbit closest to it?

19.11 Show that the total energy of a neutral hydrogen atom made up of a positively charged nucleus and an electron is given by

$$E_n = \frac{1}{n^2} E_1$$

where E_1 is the energy when the electron is in the first orbit ($n = 1$), and where the value of $E_1 = -13.6$ electron-volts. (You may consult other texts, for example *Foundation of Modern Physical Science* by Holton and Roller, sections 34.4 and 34.7.) Program and hints:

- The total energy E of the system is the kinetic and potential energy $KE + PE$ of the electron in its orbit. Since $mv^2/r = k q_e^2/r^2$ (see p. 73), $KE = \frac{1}{2}mv^2$ can be quickly calculated.
- The electrical potential energy PE of a charged point object (electron) is simply given by the electrical potential V of the region in which it finds itself, times its own charge. The value of V set up by the (positive) nucleus at distance r is given by Kq_e/r and the charge on the electron (including sign, for once!) is $-q_e$. Hence $PE = -kq_e^2/r$. The meaning of the negative sign is simply that PE is taken to be zero if the electron is infinitely distant; the system radiates energy as the electron is placed closer to the nucleus, or conversely that energy must be supplied to move the electron away from the nucleus.
- Now you can show that the total energy E is

$$E = KE + PE = -k \frac{q_e^2}{2r}$$

- Using the equation derived on p. 73, namely

$$r = \frac{n^2 h^2}{4\pi^2 m q_e^2}, \text{ show that}$$

$$E_n = -\frac{k^2 2\pi^2 m q_e^2}{n^2 h^2} = \frac{1}{n^2} E_1$$

where $E_1 = k^2 2\pi^2 m q_e^2 / h^2$.

The numerical value for this can be computed by using the known values (in consistent units) for k , m , q_e and h .

- Find the numerical value of the energy of

the hydrogen atom for each of the first 4 allowed orbits ($n = 1, 2, 3, 4$).

vi. As a final point, show that the quantity $-E_1/hc$ has the same value as the constant R_H , as claimed in Sec. 19.8.

19.12 Using the Bohr theory, how would you account for the existence of the dark lines in the absorption spectrum of hydrogen?

19.13 A group of hydrogen atoms is excited (by collision, or by absorption of a photon of proper frequency), and they all are in the stationary state for which $n = 5$. Refer to the figure in the margin on p. 78 and list all possible lines emitted by this sample of hydrogen gas.

19.14 Make an energy level diagram to represent the results of the Franck-Hertz experiment.

19.15 Many substances emit visible radiation when illuminated with ultraviolet light; this phenomenon is an example of fluorescence. Stokes, a British physicist of the nineteenth century, found that in fluorescence the wavelength of the emitted light usually was the same or longer than the illuminating light. How would you account for this phenomenon on the basis of the Bohr theory?

19.16 In Query 31 of his *Opticks*, Newton wrote:

All these things being consider'd, it seems probable to me that God in the beginning formed matter in solid, massy, hard, impenetrable, moveable particles, of such sizes and figures, and with such other properties, and in such proportion to the end for which he formed them; and that these primitive particles being solids, are incomparably harder than any porous bodies compounded of them, even so very hard, as never to wear or break in pieces; no ordinary power being able to divide what God himself made one in first the creation. While the particles continue entire, they may compose bodies of one and the same nature texture and in all ages: But should they wear away, or break in pieces, the nature of things depending on them would be changed. Water and earth, composed of old worn particles and fragments of particles, would not be of the same nature and texture now, with water and earth composed of entire particles in the beginning. And therefore that nature may be lasting, the changes of corporeal things are to be placed only in the various separations and new associations and motions of these permanent particles; compound bodies being apt to break, not in the midst of solid particles, but where those particles are laid together, and only touch in a few points.

Compare what Newton says here about atoms with

- (a) the views attributed to Leucippus and Democritus concerning atoms (see the Prologue to this unit);
- (b) Dalton's assumptions about atoms (see the end of the prologue to this unit);
- (c) the Rutherford-Bohr model of the atom

19.17 Use the chart on p. 85 to explain why atoms of potassium ($Z = 19$) have electrons in the N shell even though the M shell is not filled.

19.18 Use the chart on p. 85 to predict the atomic number of the next inert gas after argon. That is, imagine filling the electron levels with pairs of electrons until you reach an apparently stable, or complete, pattern. Do the same for the next inert gas following.

19.19 Make up a glossary, with definitions, of terms which appeared for the first time in this chapter.

19.20 The philosopher John Locke (1632-1704) proposed a science of human nature which was strongly influenced by Newton's physics. In Locke's atomistic view, elementary ideas ("atoms") are produced by elementary sensory experiences and then drift, collide and interact in the mind. Thus the association of ideas was but a special case of the universal interactions of particles.

Does such an approach to the subject of human nature seem reasonable to you? What argument for and against this sort of theory can you think of?

19.21 In a recently published textbook of physics, the following statement is made:

Arbitrary though Bohr's new postulate may seem, it was just one more step in the process by which the apparently continuous macroscopic world was being

analyzed in terms of a discontinuous, quantized, microscopic world. Although the Greeks had speculated about quantized matter (atoms), it remained for the chemists and physicists of the nineteenth century to give them reality. In 1900 Planck found it necessary to quantize the energy of electromagnetic waves. Also, in the early 1900's a series of experiments culminating in Millikan's oil-drop experiment conclusively showed that electric charge was quantized. To this list of quantized entities, Bohr added angular momentum (mvr).

- (a) What other properties or things in physics can you think of that are "quantized?"
- (b) What properties or things can you think of outside physics that might be said to be "quantized?"

19.22 Write an essay on the successes and failures of the Bohr model. Can it be called a good model? A simple model? A beautiful model?

19.23 In 1903 a philosopher wrote:

The propounders of the atomic view of electricity disagree with theories which would restrict the method of science to the use of only such quantities and data as can be actually seen and directly measured, and which condemn the introduction of such useful conceptions as the atom and the electron, which cannot be directly seen and can only be measured by indirect processes.

On the basis of the information now available to you, with which view do you agree: the view of those who think in terms of atoms and electrons, or the view that we must use only such things as can be actually seen and measured?



This construction is meant to represent the arrangement of mutually attracting sodium and chlorine ions in a crystal of common salt. Notice that the outermost electrons of the sodium atoms have been lost to the chlorine atoms, leaving positively charged sodium ions with completed K and L shells, and negatively charged chlorine ions with completed K, L and M shells.

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The diffraction pattern on the left was made by a beam of x rays passing through thin aluminum foil. The diffraction pattern on the right was made by a beam of electrons passing through the same foil.



CHAPTER TWENTY

Some Ideas from Modern Physical Theories

20.1 Some results of relativity theory

Progress in atomic and nuclear physics has been based on two great advances in physical thought: quantum theory and relativity. In so short a space as a single chapter we cannot even begin to give a coherent account of the actual development of physical and mathematical ideas in these fields. All we can do is offer you some idea of what kind of problems led to the development, suggest some of the unexpected conclusions, prepare for material in later chapters, and—very important!—introduce you to the beautiful ideas on relativity theory and quantum mechanics—offered in articles in *Reader 5*.

SG 20.1

In Chapters 18 and 19 we saw how quantum theory entered into atomic physics. To follow its further development into *quantum mechanics*, we need to learn some of the results of the relativity theory. These results will also be essential to our treatment of nuclear physics in Unit 6. We shall, therefore, devote this section to a brief discussion of one essential result of the theory of relativity introduced by Einstein in 1905—the same year in which he published the theory of the photoelectric effect.

In Unit 1 we discussed the basic idea of relativity—that certain aspects of physical events appear the same from different frames of reference, even if the reference frames are moving with respect to one another. We said there that mass, acceleration, and force seemed to be such *invariant* quantities, and Newton's laws relating them were equally good in all reference frames.

By 1905 it had become clear that this is true enough for all ordinary cases of motion, but not if the bodies involved move with respect to the observer at a speed more than a few percent of that of light. Einstein considered whether the same relativity principle could be extended to include not only the mechanics of rapidly moving bodies, but also the description of electromagnetic waves. He found this could be done by replacing Newton's definitions of length and time by others that produce a more consistent physics,

Topics in relativity theory are developed further in *Reader 5*.

See the articles:

"The Clock Paradox"

"Mr. Tompkins and Simultaneity"

"Mathematics and Relativity"

"Parable of the Surveyors"

"Outside and Inside the Elevator"

"Space Travel: Problems of Physics and Engineering"

one that resulted in a new viewpoint. The viewpoint is the most interesting part of Einstein's thinking, and parts of it are discussed in articles in *Reader 5* and *Reader 6*; but here we will deal with high-speed phenomena from an essentially Newtonian viewpoint, in terms of *corrections* required to make Newtonian mechanics a better fit to a new range of phenomena.

For bodies moving at speeds which are small compared to the speed of light, measurements predicted by relativity theory are only negligibly different from measurements predicted by Newtonian mechanics. This must be true because we know that Newton's laws account very well for the motion of the bodies with which we are familiar in ordinary life. The differences between relativistic mechanics and Newtonian mechanics become noticeable in experiments involving high-speed particles.

We saw in Sec. 18.2 that J. J. Thomson devised a method for determining the speed v and the ratio of charge to mass q_e/m for electrons. Not long after the discovery of the electron by Thomson, it was found that the value of q_e/m seemed to vary with the speed of the electrons. Between 1900 and 1910, several physicists found that electrons have the value $q_e/m = 1.76 \times 10^{11}$ coul/kg only for speeds that are very small compared to the speed of light; the ratio became smaller as electrons were given greater speeds. The relativity theory offered an explanation for these results: the electron charge is invariant—it does not depend on the speed of the electrons; but the mass of an electron, as an observer in a laboratory would measure it, should vary with speed, increasing according to the formula:

$$m = \frac{m_0}{\sqrt{1 - v^2/c^2}}$$

In this formula, v is the speed the electron has relative to the observer, c is the speed of light in a vacuum, and m_0 is the *rest mass*—the electron's mass measured by an observer when an electron is at rest with respect to the observer; m is the mass of an electron measured while it moves with speed v relative to the observer. We may call m the *relativistic mass*. It is the mass determined, for example, by means of J. J. Thomson's method.

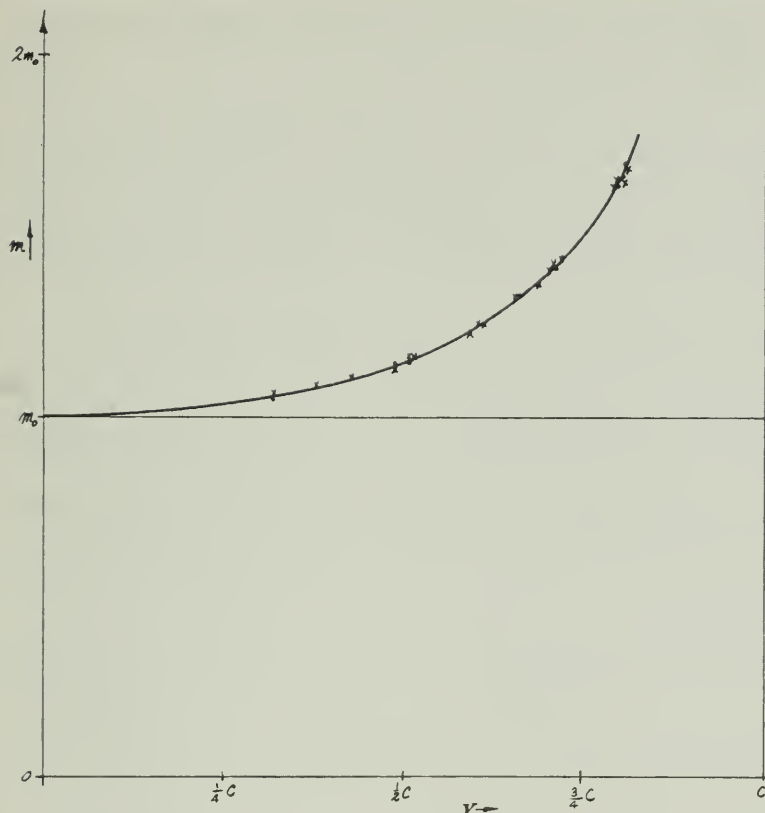
The ratio of relativistic mass to rest mass, m/m_0 , which is equal to $1/\sqrt{1 - v^2/c^2}$, is listed in the table in the margin for values of v/c which approach 1. The value of m/m_0 becomes very large as v approaches c .

The formula for the relativistic mass, which was derived by Einstein from fundamental ideas of space and time, has been tested experimentally; some of the results, for electrons with speeds so high that the value of v reaches about $0.8c$, are shown as points on the graph on the next page. At $v = 0.8c$ the relativistic mass m is about 1.7 times the rest mass m_0 . The curve shows the theoretical variation of m as the value of v increases, and the dots and crosses are results from two different experiments. The agreement of experiment and theory is excellent. The increase in mass with speed fully accounts for the shrinking of the ratio q_e/m with speed, which was mentioned earlier.

**The Relativistic Increase of
Mass with Speed**

v/c	m/m_0	v/c	m/m_0
0.0	1.000	0.95	3.203
0.01	1.000	0.98	5.025
0.10	1.005	0.99	7.089
0.50	1.155	0.998	15.82
0.75	1.538	0.999	22.37
0.80	1.667	0.9999	70.72
0.90	2.294	0.99999	223.6

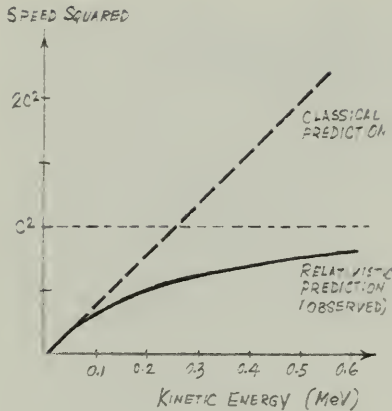
Variation of relativistic mass with speed (expressed as a fraction of the speed of light).



The formula for variation of mass with speed is valid for *all* moving bodies, not just for electrons and other atomic particles. But larger bodies, such as those with which we are familiar in everyday life, we observe at speeds so small compared to that of light that the value of v/c is very small. The value of v^2/c^2 in the denominator is then extremely small, and the values of m and m_0 are so nearly the same that we cannot tell the difference. In other words, the relativistic increase in mass can be detected in practice only for particles of atomic or sub-atomic size, those that can be given speeds higher than a small fraction of c .

SG 20.2-20.4

The effects discussed so far are mainly of historical interest because they helped to convince physicists (eventually) of the correctness of relativity theory. Experiments done more recently provide more striking evidence of the inadequacy of Newtonian physics for particles with very high speeds. Electrons can be given very high energies by accelerating them in a vacuum by means of a high voltage V . Since the electron charge q_e is known, the energy increase, $q_e v$, is known, the rest mass m_0 of an electron is also known (see Sec. 18.3), and the speed v can be measured by timing the travel over a known distance. It is, therefore, possible to compare the values of the energy supplied, $q_e V$, with the expression for kinetic energy in classical mechanics, $\frac{1}{2}m_0 v^2$. When experiments of this kind are done, it is found that when the electrons have speeds that are small compared to the speed of light, $\frac{1}{2}m_0 v^2 = q_e V$. We used this relation in Sec. 18.5 in discussing the photoelectric



Unit 6 deals further with accelerators, and the operation of the CEA apparatus is also the subject of a Project Physics film *Synchrotron*.

To increase the mass of a body by 1 gram, it would have to be given a kinetic energy of 10^{11} joules (about 6 million mile-tons).

The rest energy m_0c^2 includes the potential energy, if there is any. Thus a compressed spring has a somewhat larger rest mass and rest energy than the same spring when relaxed.

effect. We could do so quite correctly because photoelectrons do, indeed, have small speeds, and m and m_0 have nearly the same value. But when the speed of the electron becomes large, so that v/c is no longer a small fraction, it is found that the quantity $\frac{1}{2}m_0v^2$ does not increase in proportion to q_eV ; this discrepancy increases as q_eV increases. The increase in kinetic energy still is equal to the amount of work done by the electrical field, q_eV , but the mass is no longer m_0 and so kinetic energy can't be measured by $\frac{1}{2}m_0v^2$. The value of v^2 , instead of steadily increasing with energy supplied, approaches a limiting value: c^2 .

In the Cambridge Electron Accelerator (CEA) operated in Cambridge, Massachusetts, by Harvard University and the Massachusetts Institute of Technology, electrons are accelerated to an energy which is equivalent to what they would gain in being accelerated by a potential difference of 6×10^9 volts; it is an enormous energy for electrons. The speed attained by the electrons is $0.999999996 c$; at this speed the relativistic mass m (both by calculation and by experiment) is over 10,000 times greater than the rest mass m_0 !

Another way of saying mass increases with speed is this: any increase in kinetic energy is consistently accompanied by an increase in mass. If the kinetic energy measured from a frame of reference is KE , the increase in mass Δm (above the rest mass) measured in that frame is proportional to KE :

$$\Delta m \propto KE$$

But it takes a great deal of kinetic energy to give a measurable increase in mass; the proportionality constant is very small—in fact, Einstein showed it would be $1/c^2$, where c is the speed of light in a vacuum:

$$\Delta m = \frac{KE}{c^2}$$

Thus the total mass m of a body is its rest mass m_0 plus KE/c^2 :

$$m = m_0 + \frac{KE}{c^2}$$

Einstein proposed that the “mass equivalent” of kinetic energy is only a special case, and that there is in general a precise equivalence between mass and energy. Thus one might expect that the rest mass m_0 also would correspond to an equivalent amount of “rest energy” E_0 : $m_0 = E_0/c^2$. That is,

$$m = \frac{E_0}{c^2} + \frac{KE}{c^2}$$

If we use the symbol E for the *total* energy of a body, $E = E_0 + KE$, we could then write

$$m = \frac{E}{c^2}$$

This is just that Einstein concluded in 1905: “The mass of a body is a measure of its energy content.” We can write this in a more

familiar form, as what is probably the most famous equation in physics:

$$E = mc^2$$

Do not confuse E with symbol for electric field.

The last four equations all represent the same idea—that mass and energy are different expressions for the *same* characteristic of a system. It is not appropriate to think of mass being “converted” to energy or vice versa. Rather, a body with a measured mass m has an energy E equal to mc^2 ; and vice versa—a body of total energy E has a mass equal to E/c^2 .

SG 20.5, 20.6

The implications of this equivalence are exciting. First, two of the great conservation laws have become alternative statements of a single law: in any system whose total mass is conserved, the total energy will be conserved also. Second, the idea arises that some of the rest energy might be transformed into a more familiar form of energy. Since the energy equivalent of mass is so great, a very small reduction in rest mass would be accompanied by the release of a tremendous amount of energy, for example, kinetic energy or electromagnetic radiation.

In Chapters 23 and 24, we shall see how such changes come about experimentally, and see additional experimental evidence which supports this relationship.

Q1 What happens to the measurable mass of a particle as its kinetic energy is increased?

Q2 What happens to the speed of a particle as its kinetic energy is increased?

20.2 Particle-like behavior of radiation

We shall now make use of one of these relations in the further study of light quanta and of their interaction with atoms. Study of the photoelectric effect taught us that a light quantum has energy hf , where h is Planck's constant and f is the frequency of the light. This concept also applies to x rays which, like visible light, are electromagnetic radiation, but of higher frequency than visible light. The photoelectric effect, however, did not tell us anything about the *momentum* of a quantum. We may raise the question: if a light quantum has energy, does it also have momentum?

The magnitude of the momentum \vec{p} of a body is defined as the product of its mass m and speed v : $p = mv$. If we replace m with its energy equivalent E/c^2 we can write

SG 20.7

$$p = \frac{Ev}{c^2}$$

Note that the last equation is an expression for the momentum in which there is no explicit reference to mass. If we now speculate that this same equation might define the momentum of a photon of energy E , v would be replaced by the speed of light c and we would get

$$p = \frac{Ec}{c^2} = \frac{E}{c}$$

Now, $E = hf$ for a light quantum, and if we substitute this expression for E in $p = E/c$, we would get the momentum of a light quantum:

$$p = \frac{hf}{c}$$

Or, using the wave relation that the speed equals the frequency times the wavelength, $c = f\lambda$, we could express the momentum as

$$p = \frac{h}{\lambda}$$

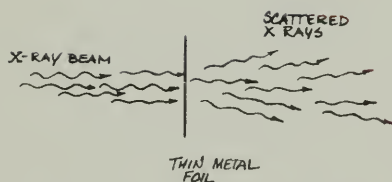
Does it make sense to define the momentum of a photon in this way? It does, if the definition is of help in understanding experimental results. The first example of the successful use of the definition was in the analysis of an effect discovered by Arthur H. Compton which we will now consider.

According to classical electromagnetic theory, when a beam of light (or x rays) strikes the atoms in a target (such as a thin sheet of metal), the light will be scattered in various directions, but its frequency will not be changed. The absorption of light of a certain frequency by an atom may be followed by re-emission of light of another frequency; but, if the light wave is simple *scattered*, then according to classical theory there should be no change in frequency.

According to quantum theory, however, light is made up of photons. Compton reasoned that if photons have momentum in accord with the argument for relativity theory, then in a collision between a photon and an atom the law of conservation of momentum should apply. According to this law (see Chapter 9), when a body of small mass collides with a massive object at rest, it simply bounces back or glances off with little loss in speed—that is, with very little change in energy. But if the masses of the two colliding objects are not very much different, a significant amount of energy can be transferred in the collision. Compton calculated how much energy a photon should lose in a collision with an atom, if the momentum of the photon is hf/c . He concluded that the change in energy is too small to observe if a photon simply bounces off an entire atom. If, however, a photon strikes an *electron*, which has a small mass, the photon should transfer a significant amount of energy to the electron.

In experiments up to 1923, no difference has been observed between the frequencies of the incident and scattered light (or x rays) when electromagnetic radiation was scattered by matter. In 1923 Compton was able to show that when a beam of x rays is scattered, the scattered beam consists of two parts: one part has the same frequency as the incident x rays; the other part has slightly lower frequency. The reduction in frequency of some of the scattered x rays is called the Compton effect. The scattered x rays of unchanged frequency have been scattered by whole atoms, whereas the component of x rays with changed frequency indicates a transfer of energy from some photons to electrons, in accordance with the laws of conservation of momentum and energy. The

SG 20.8



Arthur H. Compton (1892-1962) was born in Wooster, Ohio and graduated from the College of Wooster. After receiving his doctor's degree in physics from Princeton University in 1916, he taught physics and then worked in industry. In 1919-1920 he did research under Rutherford at the Cavendish Laboratory of the University of Cambridge. In 1923, while studying the scattering of x rays, he discovered and interpreted the changes in the wavelengths of x rays when the rays are scattered. He received the Nobel Prize in 1927 for this work.

observed change in frequency is just what would be predicted if the photons were acting like particle-like projectiles having momentum $p = hf/c$.

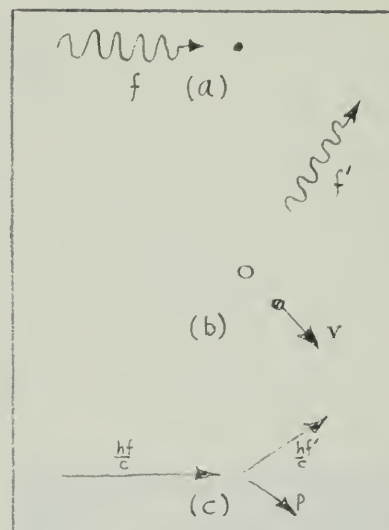
Furthermore, the electrons which were struck by the photons could also be detected, because they were knocked out of the target. Compton found that the momentum of these electrons was related to their direction in just the way that would be expected if they had been struck by particles with momentum equal to hf/c .

Compton's experiment showed that a photon can be regarded as a particle with a definite momentum as well as energy; it also showed that collisions between photons and electrons obey the laws of conservation of momentum and energy.

Photons are not like ordinary particles—if only because they do not exist at speeds other than that of light. (There can be no resting photons, and therefore no rest mass for photons.) But in other ways, as in their scattering behavior, photons act much like particles of matter, having momentum as well as energy; and they also act like waves, having frequency and wavelength. In other words, the behavior of electromagnetic radiation is in some experiments similar to what we are used to thinking of as particle behavior, and in other experiments is similar to what we are used to thinking of as wave behavior. This behavior is often referred to as the *wave-particle dualism of radiation*. The question, “Is a photon a wave or a particle?” can only be answered: it can *act* like either, depending on what we are doing with it. (This fascinating topic is elaborated in several of the *Reader 5* articles.)

Q3 How does the momentum of a photon depend on the frequency of the light?

Q4 What is the Compton effect, and what did it prove?



SG 20.9

SG 20.10

20.3 Wave-like behavior of particles

In 1923, the French physicist Louis de Broglie suggested that the wave-particle dualism which applies to radiation might also apply to electrons and other atomic particles. Perhaps, he said, the wave-particle dualism is a fundamental property of all quantum processes, and what we have always thought of as material particles can, in some circumstances, act like waves. He sought an expression for the wavelength that might be associated with wave-like behavior of an electron, and he found one by means of a simple argument.

The momentum of a photon of wavelength λ is $p = h/\lambda$. De Broglie suggested that this relation, derived for photons, would also apply to electrons with the momentum $p = mv$. He therefore boldly suggested that the wavelength of an electron is:

$$\lambda = \frac{h}{mv}$$

where m is the mass of the electron and v its speed.

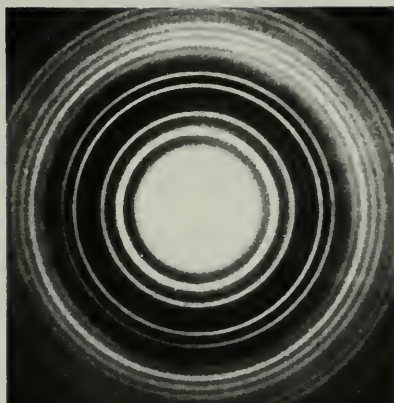
What does it mean to say that an electron has a wavelength equal to Planck's constant divided by its momentum? If this

The “de Broglie wavelength” of a material particle does not refer to anything having to do with light, but to some new wave property associated with the motion of matter itself.

statement is to have any physical meaning, it must be possible to test it by some kind of experiment. Some wave property of the electron must be measured. The first such property to be measured was *diffraction*.

The relationship $\lambda = h/mv$ implies that the wavelengths associated with electrons will be very short, even for fairly slow electrons; an electron accelerated across a potential difference of only 100V would have a wavelength of only 10^{-10} meter. So small a wavelength would not give noticeable diffraction effects on encountering any object of appreciable size—even microscopically small size (say, 10^{-5} meter).

By 1920 it was known that crystals have a regular lattice structure; the distance between rows or planes of atoms in a crystal is about 10^{-10} m. After de Broglie proposed his hypothesis that electrons have wave properties, several physicists suggested that the existence of electron waves might be shown by using crystals as diffraction gratings. Experiments begun in 1923 by C. J. Davisson and L. H. Germer in the United States, yielded diffraction patterns similar to those obtained for x rays (see Sec. 18.6) as illustrated in the two drawings at the left below. The experiment showed two things: first that electrons do have wave properties—one may say that an electron moves along the path taken by the de Broglie wave that is associated with the electron. Also, it showed that their wavelengths are correctly given by de Broglie's relation, $\lambda = h/mv$. These results were confirmed in 1927 by G. P. Thomson, who directed an electron beam through thin gold foil to produce a pattern like the one in the margin, similar to diffraction patterns produced by light beams going through thin slices of materials. By 1930, diffraction from crystals had been used to demonstrate the wave-like behavior of helium *atoms* and hydrogen *molecules*, as illustrated in the drawing on page 103.



Diffraction pattern produced by directing a beam of electrons through polycrystalline aluminum. With a similar pattern, G. P. Thomson demonstrated the wave properties of electrons—28 years after their *particle* properties were first demonstrated by J. J. Thomson, his father.

The de Broglie wavelength: examples.

A body of mass 1 kg moves with a speed of 1 m/sec. What is its de Broglie wavelength?

$$\lambda = \frac{h}{mv}$$

$$h = 6.6 \times 10^{-34} \text{ joule}\cdot\text{sec}$$

$$mv = 1 \text{ kg}\cdot\text{m/sec}$$

$$\lambda = \frac{6.6 \times 10^{-34} \text{ joule}\cdot\text{sec}}{1 \text{ kg}\cdot\text{m/sec}}$$

so

$$\lambda = 6.6 \times 10^{-34} \text{ m}$$

The de Broglie wavelength is many orders of magnitude smaller than an atom, and so is much too small to be detected—there are, for example, no slits or obstacles small enough to show diffraction effects. We would expect to detect no wave aspects in the motion of this body.

An electron of mass 9.1×10^{-31} kg moves with a speed of 2×10^6 m/sec. What is its de Broglie wavelength?

$$\lambda = \frac{h}{mv}$$

$$h = 6.6 \times 10^{-34} \text{ joule}\cdot\text{sec}$$

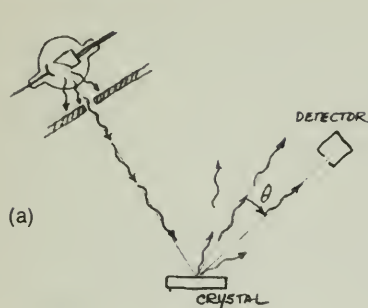
$$mv = 1.82 \times 10^{-24} \text{ kg}\cdot\text{m/sec}$$

$$\lambda = \frac{6.6 \times 10^{-34} \text{ joule}\cdot\text{sec}}{1.82 \times 10^{-24} \text{ kg}\cdot\text{m/sec}}$$

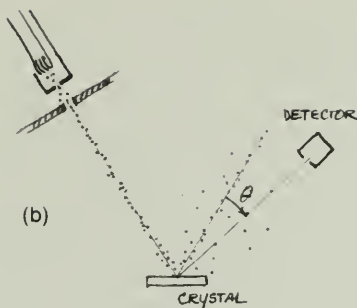
so

$$\lambda = 3.6 \times 10^{-10} \text{ m}$$

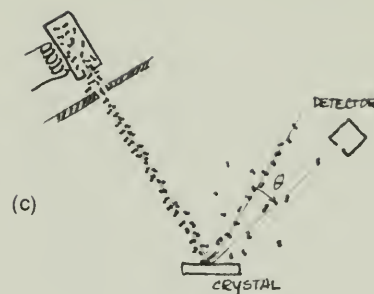
The de Broglie wavelength is of atomic dimensions; for example, it is of the same order of magnitude as the distances between atoms in a crystal. So we expect to see wave aspects in the interaction of electrons with crystals.



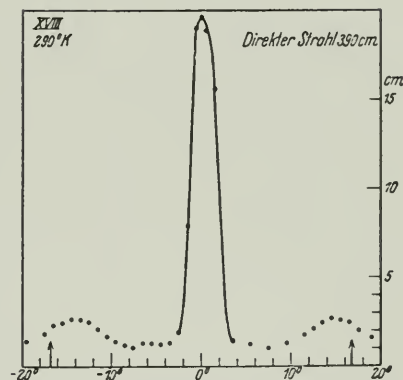
a. One way to demonstrate the wave behavior of x rays is to direct a beam at the surface of a crystal. The reflections from different planes of atoms in the crystal interfere to produce reflected beams at angles other than the ordinary angle of reflection.



b. A very similar effect can be demonstrated for a beam of electrons. The electrons must be accelerated to an energy that corresponds to a de Broglie wavelength of about 10^{-10} m (which requires an accelerating voltage of only about 100 volts).



c. Like any other beam of particles, a beam of molecules directed at a crystal will show a similar diffraction pattern. The diagram above shows how a beam of hydrogen molecules (H_2) can be formed by slits at the opening of a heated chamber; the average energy of the molecules is controlled by adjusting the temperature of the oven. The graph, reproduced from *Zeitschrift für Physik*, 1930, shows results obtained by I. Estermann and O. Stern in Germany. The detector reading is plotted against the deviation to either side of the angle of ordinary reflection.



Diffraction pattern for H_2 molecules glancing off a crystal of lithium fluoride.

According to de Broglie's hypothesis, which has been confirmed by all experiments, wave-particle dualism is a general property not only of radiation but also of matter. It is now customary to use the word "particle" to refer to electrons and photons while recognizing that they both have properties of waves as well as of particles (and, of course, that there are important differences between them).

De Broglie's relation, $\lambda = h/mv$, has an interesting yet simple application which makes more reasonable Bohr's postulate that the quantity mvr (the angular momentum) of the electron in the hydrogen atom can only have certain values. Bohr assumed that mvr can have only the values:

$$mvr = n \frac{h}{2\pi} \text{ where } n = 1, 2, 3, \dots$$

Now, suppose that an electron wave is somehow spread over an orbit of radius r —that, in some sense, it "occupies" an orbit of radius r . We may ask if *standing waves* can be set up as indicated, for example, in the sketch in the margin. The condition for such standing waves is that the circumference of the orbit is equal in length to a whole number of wavelengths, that is, to $n\lambda$. The mathematical expression for this condition of "fit" is:

$$2\pi r = n\lambda$$

SG 20.11–20.13

Only certain wavelengths will "fit" around a circle.



If we now replace λ by h/mv according to de Broglie's relation we get

$$2\pi r = n \frac{h}{mv}$$

or

$$mvr = n \frac{h}{2\pi}$$

SG 20.14

But, this is just Bohr's quantization condition! The de Broglie relation for electron waves – and the idea that the electron is in orbits that allow a standing wave – allows us to *derive* the quantization that Bohr had to *assume*.

The result obtained indicates that we may picture the electron in the hydrogen atom in two ways: either as a particle moving in an orbit with a certain quantized value of mvr , or as a standing de Broglie-type wave occupying a certain region around the nucleus.

Either way is incomplete by itself.

Q5 Where did de Broglie get the relation $\lambda = h/mv$ for electrons?

Q6 Why were crystals used to get diffraction patterns of electrons?

20.4 Mathematical vs. visualizable atoms

The proof that “things” (electrons, atoms, molecules) which had been regarded as particles also show properties of waves has served as the basis for the currently accepted theory of atomic structure. This theory, *quantum mechanics*, was introduced in 1925; its foundations were developed with great rapidity during the next few years, primarily by Heisenberg, Born, Schrödinger, Bohr, and Dirac. Initially the theory appeared in two different mathematical forms, proposed independently by Heisenberg and Schrödinger. A few years later, these two forms were shown by Dirac to be equivalent, different ways of expressing the same relationships. The form of the theory that is closer to the ideas of de Broglie, discussed in the last section, was that of Schrödinger. It is often referred to as “wave mechanics”.

One of the fundamental requirements for a physical theory is that it predict the path taken by a particle when it interacts with other particles. It is possible, as we have already indicated for light, to write an equation describing the behavior of waves that will imply the path of the waves – the “rays.”

Schrödinger sought to express the dual wave and particle nature of matter mathematically. Maxwell had formulated the electromagnetic theory of light in terms of a wave equation, and physicists were familiar with this theory and its applications. Schrödinger reasoned that the de Broglie waves associated with electrons would resemble the classical waves of light, including also that there be a wave equation that holds for matter waves just as there is a wave equation for electromagnetic waves. We cannot discuss this mathematical part of wave mechanics even adequately without using an advanced part of mathematics, but the physical ideas

involved require only a little mathematics and are essential to an understanding of modern physics. So, in the rest of this chapter, we shall discuss some of the physical ideas of the theory to try to make them seem plausible; and we shall consider some of the results of the theory and some of the implications of these results. But again our aim is not (and cannot honestly be in the available time and space) a full presentation. We want only to prepare for the use of specific results, and for reading in *Reader 5* and *Reader 6*.

Schrödinger was successful in deriving an equation for the waves presumed to “guide” the motion of electrons. This equation, which has been named after him, defines the wave properties of electrons and also predicts particle-like behavior. The Schrödinger equation for an electron bound in an atom has a solution only when a constant in the equation has the whole-number values 1, 2, 3. . . . It turns out that these numbers correspond to different energies, so the Schrödinger equation predicts that only certain electron energies are possible in an atom. In the hydrogen atom, for example, the single electron can only be in those states for which the energy of the electron has the values:

$$E_n = \frac{2\pi^2mq_e^4}{n^2h^2}$$

with n having only whole number values. But these values of the energies are what are found experimentally—and are just the ones given by the Bohr theory! In Schrödinger’s theory, this result follows directly from the mathematical formulation of the wave and particle nature of the electron. The existence of these stationary states has not been assumed, and no assumptions have been made about orbits. The new theory yields all the results of the Bohr theory without having any of the inconsistent hypotheses of the earlier theory. The new theory also accounts for the experimental information for which the Bohr theory failed to account, such as the probability of an electron changing from one energy state to another.

On the other hand, quantum mechanics does not supply a physical model or visualizable picture of what is going on in the world of the atom. The planetary model of the atom has had to be given up, and has not been replaced by another simple picture. There is now a highly successful *mathematical* model, but no easily visualized *physical* model. The concepts used to build quantum mechanics are more abstract than those of the Bohr theory; it is hard to get an intuitive feeling for atomic structure without training in the field. But the mathematical theory of quantum mechanics is much more powerful than the Bohr theory, in predicting and explaining phenomena, and many problems that were previously unsolvable have been solved with quantum mechanics. Physicists have learned that the world of atoms, electrons, and photons cannot be thought of in the same mechanical terms as the world of everyday experience. The world of atoms has presented us with some fascinating concepts which will be discussed in the next two sections; what has been lost in easy visualizability is amply made up for by the increased range of fundamental understanding.

Topics in quantum physics are developed further in *Reader 5*.

See the articles:

“Ideas and Theories”

“The New Landscape of Science”

“The Evolution of the Physicist’s

Picture of Nature”

“Dirac and Born”

“I am the Whole World: Erwin Schrödinger”

“The Fundamental Idea of Wave Mechanics”

“The Sea-Captain’s Box”

Visualizability is an unnecessary luxury when it is bought at the cost of clarity. For the same reason we learned to do without visualizability in many other fields. For example, we no longer think of the action of an ether to explain light propagation. (Nor do we demand to see pieces of silver or gold or barter goods when we accept a check as payment.)



P. A. M. Dirac (1902-), an English physicist, was one of the developers of modern quantum mechanics. In 1932, at the age of 30, Dirac was appointed Lucasian Professor of Mathematics at Cambridge University, the post held by Newton.



Max Born (1882-1969) was born in Germany, but left that country for England in 1933 when Hitler and the Nazis gained control. Born was largely responsible for introducing the statistical interpretation of wave mechanics.



Erwin Schrödinger (1887-1961) was born in Austria. He developed wave mechanics in 1926, fled from Germany in 1933 when Hitler and the Nazis came to power. From 1940 to 1956, when he retired, he was professor of physics at the Dublin Institute for Advanced Studies.

Prince Louis Victor de Broglie (1892-) comes of a noble French family. His ancestors served the French kings as far back as the time of Louis XIV. He was educated at the Sorbonne in Paris, and proposed the idea of wave properties of electrons in his PhD thesis.



Werner Heisenberg (1901-), a German physicist, was one of the developers of modern quantum mechanics (at the age of 23). He first stated the uncertainty principle, and after the discovery of the neutron in 1932, proposed the proton-neutron theory of nuclear structure.

Q7 The set of energy states of hydrogen could be derived from Bohr's postulate that $mvr = nh/2\pi$. In what respect was the derivation from Schrödinger's equation better?

Q8 Quantum (or wave) mechanics has had great success. What is its drawback for those trained on physical models?

20.5 The uncertainty principle

Up to this point we have always talked as if we could measure any physical property as accurately as we pleased; to reach any desired degree of accuracy we would have only to design a sufficiently precise instrument. Wave mechanics showed, however, that even in thought experiments with ideal instruments there are limitations on the accuracy with which measurements can be made.

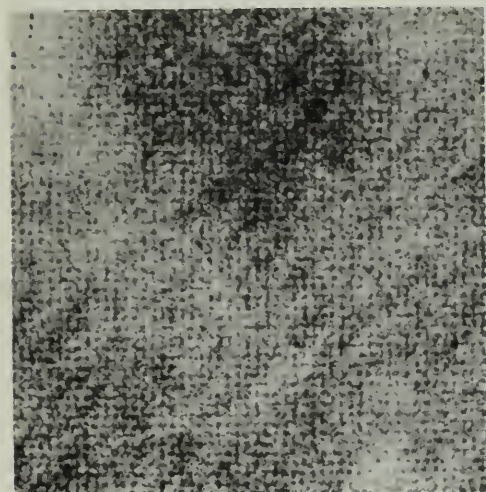
Think how you would go about measuring the positions and velocity of a car that moves slowly along a driveway. We can mark the position of the front end of the car at a given instant by making a scratch on the ground; at the same time, we start a stop-watch. Then we can run to the end of the driveway, and at the instant that the front end of the car reaches another mark placed on the ground we stop the watch. We then measure the distance between the marks and get the average speed of the car by dividing the measured distance traversed by the measured time elapsed. Since we know the direction of the car's motion, we know the average velocity. Thus we know that at the moment the car reached the second mark it was at a certain distance from its starting point and had traveled at a certain average velocity. By the process of going to smaller and smaller intervals we could also get the instantaneous velocity at any point along its path.

How did we get the needed information? We located the position of the car by sunlight bounced off the front end into our eyes; that permitted us to see when the car reached a certain mark on the ground. To get the average speed we had to locate the front end twice.

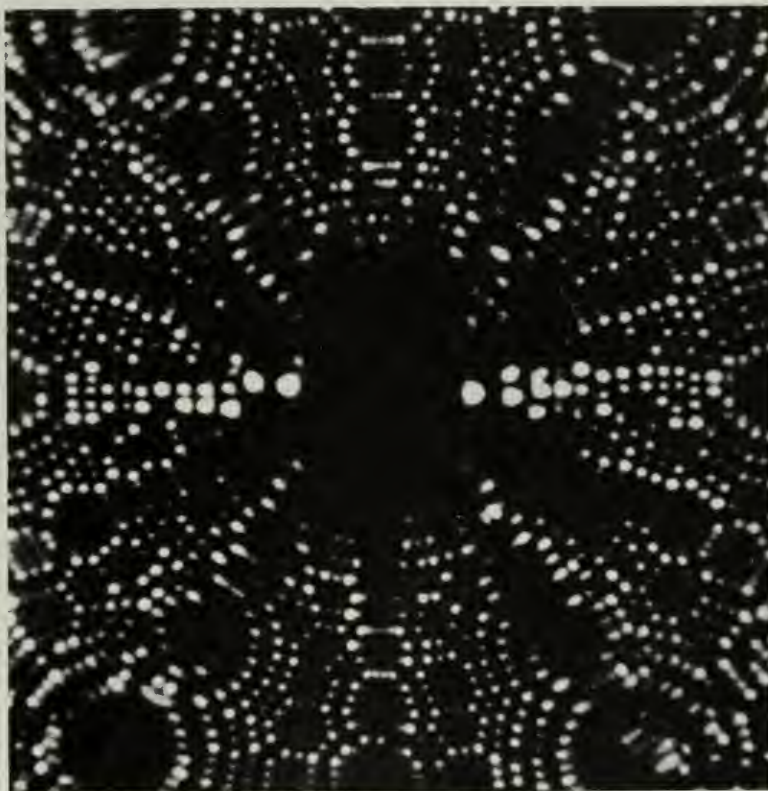
But suppose that we had decided to use reflected radio waves instead of light of visible wavelength. At 1000 kilocycles per second, a typical value for radio signals, the wavelength is 300 meters. With radiation of this wavelength, which is very much greater than the dimensions of the car, it is impossible to locate the car with any accuracy. The wave would reflect from the car ("scatter" is a more appropriate term) in all directions, just as it would sweep around any man-sized device we used to detect the wave direction. The wavelength has to be comparable with or smaller than the dimensions of the object before the object can be located well. *Radar* uses wavelengths from about 0.1 cm to about 3 cm; so a radar apparatus could have been used instead of sunlight, but would leave uncertainties as large as several centimeters in the two measurements of position. With visible light whose wavelength is less than 10^{-6} m, we could design instruments that would locate the position of the car to an accuracy of a few thousandths of a millimeter.

$$\lambda = \frac{c}{f} = \frac{3 \times 10^8 \text{ m/sec}}{10^6 \text{ /sec}} = 300 \text{ m}$$

The extreme smallness of the atomic scale is indicated by these pictures made with techniques that are near the very limits of magnification—about 10,000,000 times in these reproductions.



Pattern produced by electron beam scattered from a section of a single gold crystal. The entire section of crystal shown is only 100\AA across—smaller than the shortest wavelength of ultraviolet light that could be used in a light microscope. The finest detail that can be resolved with this “electron microscope” is just under 2\AA , so the layers of gold atoms (spaced slightly more than 2\AA) show as a checked pattern; individual atoms are beyond the resolving power.



Pattern produced by charged particles repelled from the tip of a microscopically thin tungsten crystal. The entire section shown is only about 100\AA across. The finest detail that can be revealed by this “field-ion microscope” is about 1\AA , but the bright spots indicate the locations of atoms along edges of the crystal, and should not be thought of as pictures of the atoms.

Let us now turn from car and driveway, and think of an electron moving across an evacuated tube. We shall try to measure the position and speed of the electron. But some changes have to be made in the method of measurement. The electron is so small that we cannot locate its position by using visible light: the wavelength of visible light, small as it is, is still at least 10^4 times greater than the diameter of an atom.

To locate an electron within a region the size of an atom (about 10^{-10} m across) we must use a light beam whose wavelength is comparable to the size of the atom, preferably smaller. Now a photon of such a short wavelength λ (and high frequency f) has very great momentum (h/λ) and energy (hf); and, from our study of the Compton effect, we know that the photon will give the electron a strong kick when it is scattered by the electron. As a result, the velocity of the electron will be greatly changed, into a new and unknown direction. (This is a new problem, one we did not even think about when speaking about measuring the position of the car!) Hence, when we receive the scattered photon we can deduce from its direction where the electron had been—and so we have “located” the electron. But in the process we have altered the velocity of the electron (in both magnitude and direction).

To say this more directly: the more accurately we locate the electron (by using photons of shorter wavelength) the less accurately we can know its velocity. We could try to disturb the electron less by using less energetic photons. But because light exists in quanta of energy hf , a *lower-energy* photon will have a *longer* wavelength—and therefore would give us greater uncertainty in the electron's *position*!

To summarize: *we are unable to measure both the position and velocity of an electron to unlimited accuracy*. This conclusion is expressed in the *uncertainty principle*, and was first stated by Werner Heisenberg. The uncertainty principle can be expressed quantitatively in a simple formula, derived from Schrödinger's wave equation for the motion of particles. If Δx is the uncertainty in position, and Δp is the uncertainty in momentum, then the product of the two uncertainties must be equal to, or greater than, Planck's constant divided by 2π :

$$\Delta x \Delta p \geq \frac{h}{2\pi}$$

The same reasoning (and equation) holds for the experiment on the car, but the limitation is of no practical consequence with such a massive object. (See the worked-out example below.) It is only on the atomic scale that the limitation becomes evident and important.

SG 20.16–20.18

The uncertainty principle: examples

A large mass.

Consider a car, with a mass of 1000 kg, moving with a speed of about 1 m/sec. Suppose that in this experiment the inherent uncertainty Δv in the measured speed is 0.1 m/sec (10% of the speed). What is the uncertainty in the position of the car?

$$\Delta x \Delta p \geq \frac{h}{2\pi}$$

$$\Delta p = m \Delta v = 100 \text{ kg} \cdot \text{m/sec}$$

$$h = 6.63 \times 10^{-34} \text{ joule} \cdot \text{sec}$$

$$\Delta x \geq \frac{6.63}{6.28} \frac{10^{-34} \text{ joule} \cdot \text{sec}}{10^2 \text{ kg} \cdot \text{m/sec}}$$

$$\Delta x \geq 1 \times 10^{-36} \text{ m.}$$

This uncertainty in position—many of orders smaller than the size of atoms—is much too small to be observable. In this case we can determine the position of the body with as high an accuracy as we would ever need.

A small mass.

Consider an electron, with a mass of 9.1×10^{-31} kg, moving with a speed of about 2×10^6 m/sec. Suppose that the uncertainty Δv in the speed is 0.2×10^6 m/sec (10% of the speed). What is the uncertainty in the position of the electron?

$$\Delta x \Delta p \geq \frac{h}{2\pi}$$

$$\Delta p = m \Delta v = 1.82 \times 10^{-25} \text{ kg} \cdot \text{m/sec}$$

$$h = 6.63 \times 10^{-34} \text{ joule} \cdot \text{sec}$$

$$\Delta x \geq \frac{6.63}{6.28} \times \frac{10^{-34} \text{ joule} \cdot \text{sec}}{1.82 \times 10^{-25} \text{ kg} \cdot \text{m/sec}}$$

$$\Delta x \geq 5 \times 10^{-10} \text{ m.}$$

The uncertainty in position is of the order of atomic dimensions, and is significant in atomic problems. It is impossible to specify where an electron is in an atom.

The reason for the difference between these two results is that Planck's constant h is very small; so small that the uncertainty principle becomes important only on the atomic scale. Ordinary objects behave as if, in the equations used here, h is effectively equal to zero.

The chief use made of the uncertainty principle is in general arguments in atomic theory rather than in particular numerical problems. We do not really need to know exactly where an electron is, but we sometimes want to know if it *could* be in some *region* of space.

Q9 If photons used in finding the velocity of an electron disturb the electron too much, why cannot the observation be improved by using less energetic photons?

Q10 If the wavelength of light used to locate a particle is too long, why cannot the location be found more precisely by using light of shorter wavelength?

These sketches represent greatly enlarged images of a distant star on a photographic plate.



A



B



C

To explore further the implications of dualism we need to review some ideas of probability. Even in situations in which no single event can be predicted with certainty, it may still be possible to make predictions of the statistical probabilities of certain events. On a holiday weekend during which perhaps 25 million cars are on the road, the statisticians report a high probability that about 600 people will be killed in accidents. It is not known which cars in which of the 50 states will be the ones involved in the accidents, but on the basis of past experience the average behavior is still quite accurately predictable.

It is in this way that physicists think about the behavior of photons and material particles. As we have seen, there are fundamental limitations on our ability to describe the behavior of an individual particle. But the laws of physics often enable us to describe the behavior of large collections of particles with good accuracy. The solutions of Schrödinger's wave equations for the behavior of waves associated with particles give us the *probabilities* for finding the particles at a given place at a given time.

To see how probability fits into the picture, consider the situation of a star being photographed through a telescope. As you have already seen (for example on the page on Diffraction and Detail in Chapter 13), the image of a point source is not a precise point but is a *diffraction pattern*—a central spot with a series of progressively fainter circular rings.

The image of a star on the photographic film in the telescope would be a similar pattern. Imagine now that we wished to photograph a very faint star. If the energy in light rays were not quantized, but spread continuously over ever-expanding wave fronts, we would expect that the image of a very faint star would be exactly the same as that of a much brighter star—except that the intensity of light would be less over the whole pattern. However, the energy of light is quantized—it exists in separate quanta, “photons,” of definite energy. When a photon strikes a photographic emulsion, it produces a chemical change in the film at a single location—not all over the image area. If the star is very remote, only a few photons per second may arrive at the film. The effect on the film after a very short period of exposure would not be at all like the diffraction pattern in drawing C in the margin, but something like the scatter in A. As the exposure continued, the effect on the film would begin to look like B. Eventually, a pattern like C would be produced, just like the image produced by a bright star with a much shorter exposure.

If there are tremendous numbers of quanta, then their overall distribution will be very well described by the distribution of wave intensity. For small numbers of quanta, the wave intensity will not be very useful for predicting where they will go. We expect them to go mostly to the “high-intensity” parts of the image but we cannot predict exactly where. These facts fit together beautifully if we consider the wave intensity at a location to indicate the *probability* of the photon going there!

A similar connection can be made for de Broglie waves and particles of matter. Rather than considering an analogous example, such as a diffraction pattern formed by an electron beam, we can consider a bound electron wave—a wave confined to a region of space by the electric attraction of a positive nucleus and a negative electron. For example, the de Broglie wave associated with an electron is spread out all over an atom—but we need not think of the *electron* as spread out. It is quite useful to think of the electron as a particle moving around the nucleus, and the wave amplitude at some location represents the *probability* of the electron being there.

According to modern quantum theory, the hydrogen atom does not consist of a localized negative particle moving around a nucleus as in the Bohr model. Indeed, the theory does not provide any picture of the hydrogen atom. A description of the probability distribution is the closest thing that the theory provides to a picture. The probability distribution for the lowest energy state of the hydrogen atom is represented in the drawing at the left below, where whiter shading at a point indicates greater probability. The probability distribution for a higher energy state, still for a single electron, is represented in the drawing at the right.

Quantum theory is, however, not really concerned with the position of any individual electron in any individual atom. Instead, the theory gives a mathematical representation that can be used to predict interaction with particles, fields, and radiation. For example, it can be used to calculate the probability that hydrogen will emit light of a particular wavelength; the intensity and wavelength of light emitted by a large number of hydrogen atoms can then be compared with these calculations. Comparisons such as these have shown that the theory agrees with experiment.

As we have already discussed in connection with kinetic theory and disorder, it is easy to predict the average behavior of very large numbers of particles, even though nothing at all is known about the behavior of any single one of them.



To understand atomic physics, we deal with the average behavior of many atomic particles; the laws governing this average behavior turn out to be those of wave mechanics. The waves, it seems, are waves that measure probability. The information about the probability (that a particle will have some position at a given time) travels through space in waves. These waves can interfere with each other in exactly the same way that water waves do. So, for example, if we think of a beam of electrons passing through two slits, we consider the electrons to be waves and compute the interference patterns which determine the directions in which there are high wave amplitudes (high probability of electrons going there). Then, as long as there are no more slits or other interactions of the waves with matter, we can return to our description in terms of particles and say that the electrons are likely to (and on the average will) end up going in such and such directions with such and such speeds.

The success of wave mechanics emphasized the importance of the dual wave-and-particle nature of radiation and matter. But it is natural to ask how a particle can be thought of as “really” having wave properties. The answer is that matter, particularly on the scale of the atom, does not have to be thought of as being either “really” particles or “really” waves. Our ideas of waves and of particles are taken from the world of visible things and just do not apply on the atomic scale.

When we try to describe something that no one has ever seen or can ever see directly, it would be surprising if the concepts of the visible world could be used unchanged. It appeared natural before 1925 to try to talk about the transfer of energy in either wave terms or particle terms, because that was all physicists needed or knew at the time. Almost no one was prepared to find that *both* wave and particle descriptions could apply to light and to matter. But as long as our imagination and language has only these two ideas—waves and particles—to stumble along on, this dualism cannot be wished away; it is the best way to handle experimental results.

Max Born, one of the founders of quantum mechanics, has written:

The ultimate origin of the difficulty lies in the fact (or philosophical principle) that we are compelled to use the words of common language when we wish to describe a phenomenon, not by logical or mathematical analysis, but by a picture appealing to the imagination. Common language has grown by everyday experience and can never surpass these limits. Classical physics has restricted itself to the use of concepts of this kind; by analyzing visible motions it has developed two ways of representing them by elementary processes: moving particles and waves. There is no other way of giving a pictorial description of motions—we have to apply it even in the region of atomic processes, where classical physics breaks down.

See “Dirac and Born” in *Reader 5*.

Despite the successes of the idea that the wave represents the

SG 20.23

probability of finding its associated particle in some specific condition of motion, many scientists found it hard to accept the idea that men cannot know exactly what any one particle is doing. The most prominent of such disbelievers was Einstein. In a letter to Born written in 1926, he remarked:

The quantum mechanics is very imposing. But an inner voice tells me that it is still not the final truth. The theory yields much, but it hardly brings us nearer to the secret of the Old One. In any case, I am convinced that He does not play dice.

“Deterministic” means here that if all the conditions of an isolated system are known and the laws describing interaction are known, then it is possible to predict precisely what happens next, without any need for probability ideas.

SG 20.19–20.23

Thus, Einstein, while agreeing with the usefulness and success of wave mechanics so interpreted, refused to accept probability-based laws as the final level of explanation in physics; in the remark about not believing that God played dice—an expression he used many times later—he expressed his faith that there are more basic, deterministic laws yet to be found. Yet despite the refusal of Einstein (and some others) to accept the probability laws in mechanics, neither he nor other physicists have yet succeeded in replacing Born’s probability interpretation of quantum mechanics.

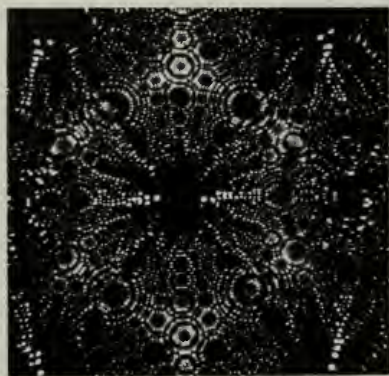
Scientists agree that quantum mechanics works; it gives the right answers to many questions in physics, it unifies ideas and occurrences that were once unconnected, and it has been wonderfully productive of new experiments and new concepts. On the other hand, there is still vigorous argument about its basic significance. It yields probability functions, not precise trajectories. Some scientists see in this aspect of the theory an important revelation about the nature of the world; for other scientists this same fact indicates that quantum theory is incomplete. Some in this second group are trying to develop a more basic, non-statistical theory for which the present quantum theory is only a limiting case. As in other fields of physics, the greatest discoveries here may be those yet to be made.

Q11 In wave terms, the bright lines of a diffraction pattern are regions where there is a high field intensity produced by constructive interference. What is the probability interpretation of quantum mechanics for the bright lines of a diffraction pattern?

Q12 If quantum mechanics can predict only probabilities for the behavior of any one particle, how can it predict many phenomena, for example, half-lives and diffraction patterns, with great certainty?



"Sea and Sky", by M. C. Escher



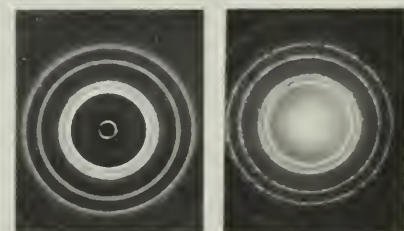
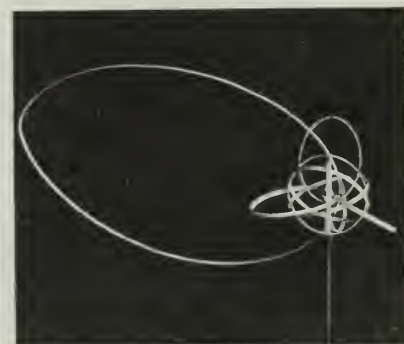
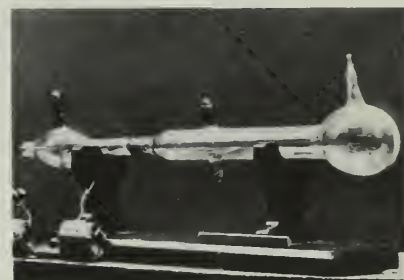
EPILOGUE In this unit we have traced the concept of the atom from the early ideas of the Greeks to the quantum mechanics now generally accepted by physicists. The search for the atom started with the qualitative assumptions of Leucippus and Democritus who thought that their atoms offered a rational explanation of the behavior of matter. For many centuries most natural philosophers thought that other explanations, not involving atoms, were more reasonable. Atomism was pushed aside and received only occasional consideration until the seventeenth century. With the growth of the mechanical philosophy of nature in the seventeenth and eighteenth centuries, particles (corpuscles) became important. Atomism was reexamined, mostly in connection with physical properties of matter. Galileo, Boyle, Newton and others speculated on the role of particles for explaining the expansion and contraction of gases. Chemists speculated about atoms in connection with chemical change. Finally, Dalton began the modern development of atomic theory, introducing a quantitative conception that had been lacking—the relative atomic mass.

Chemists, in the nineteenth century, found that they could correlate the results of many chemical experiments in terms of atoms and molecules. They also found that there are relations between the properties of different chemical elements. Quantitative information about atomic masses provided a framework for the system organizing these relations—the periodic table of Mendeleev. During the nineteenth century, physicists developed the kinetic theory of gases. This theory—based on the assumption of very small corpuscles, or particles, or

molecules, or whatever else they might be called—helped strengthen the position of the atomists. Other work of nineteenth-century physicists helped pave the way to the study of the structure of atoms—through the study of the spectra of the elements and of the conduction of electricity in gases, the discovery of cathode rays, electrons, and x rays.

Nineteenth-century chemistry and physics converged, at the beginning of the twentieth century, on the problem of atomic structure. It became clear that the uncuttable, infinitely hard atom was too simple a model: that the atom itself is made up of smaller particles. And so the search for a model with structure began. Of the early models, that of Thomson gave way to Rutherford's nuclear atom, with its small, heavy, positively charged nucleus, surrounded somehow by negative charges. Then came the atom of Bohr, with its electrons thought to be moving in orbits like planets in a miniature solar system. The Bohr theory had many successes and linked chemistry and spectra to the physics of atomic structure. But beyond that, it could not advance substantially without giving up an easily grasped picture of the atom. The tool needed is the mathematical model, not pictures. Quantum mechanics enables us to calculate how atoms behave; it helps us understand the physical and chemical properties of the elements. But at the most basic level, nature still has secrets.

The next stage in our story, Unit 6, is the nucleus at the center of the atom. Is the nucleus made up of smaller components? Does it have laws of physics all its own?



20.1 The Project Physics materials particularly appropriate for Chapter 20 include:

Activities

- Standing waves on a band-saw blade
- Turntable oscillator patterns resembling de Broglie waves
- Standing waves in a wire ring

Reader Articles

- The Clock Paradox
- Ideas and Theories
- Mr. Tompkins and Simultaneity
- Mathematics and Relativity
- Parable of the Surveyors
- Outside and Inside the Elevator
- Einstein and Some Civilized Discontents
- The New Landscape of Science
- The Evolution of the Physicist's Picture of Nature
- Dirac and Born
- I am the Whole World: Erwin Schrödinger
- The Fundamental Idea of Wave Mechanics
- The Sea-Captain's Box
- Space Travel: Problems of Physics and Engineering
- Looking for a New Law

20.2 How fast would you have to move to increase your mass by 1%?

20.3 The centripetal force on a mass moving with relativistic speed v around a circular orbit of radius R is $F = mv^2/R$, where m is the relativistic mass. Electrons moving at a speed $0.60c$ are to be deflected in a circle of radius 1.0 m : what must be the magnitude of the force applied? ($m_0 = 9.1 \times 10^{-31}\text{ kg}$.)

20.4 The formulas ($p = m_0v$, $KE = \frac{1}{2}m_0v^2$) used in Newtonian physics are convenient approximations to the more general relativistic formulas. The factor $1/\sqrt{1 - v^2/c^2}$ can be expressed as an infinite series of steadily decreasing terms by using a binomial series expansion. When this is done we find that

$$\frac{1}{\sqrt{1 - \frac{v^2}{c^2}}} = 1 + \frac{1}{2} \frac{v^2}{c^2} + \frac{3}{8} \frac{v^4}{c^4} + \frac{5}{16} \frac{v^6}{c^6} + \dots$$

- (a) Show, by simple substitution, that when $\frac{v}{c}$ is less than 0.1 , the values of the terms drop off so rapidly that only the first few terms need be considered.
- (b) We rarely observe familiar objects moving faster than about $3,000\text{ m/sec}$; the speed of light is $3 \times 10^8\text{ m/sec}$, so the value of v/c for familiar objects is rarely greater than about 10^{-5} . What error do we suffer by using only the first two terms of the series?
- (c) Substitute the first two terms of the series into the relativistic expression

and show that $KE = \frac{1}{2}m_0v^2$ is a good approximation for familiar objects.

20.5 According to relativity theory, changing the energy of a system by ΔE also changes the mass of the system by $\Delta m = \Delta E/c^2$. Something like 10^5 joules per kilogram of substance are commonly released as heat energy in chemical reactions.

- (a) Why then aren't mass changes detected in chemical reactions?
- (b) Calculate the mass change associated with a change of energy of 10^5 joules.

20.6 The speed of the earth in its orbit is about 18 miles/sec ($3 \times 10^4\text{ m/sec}$). Its "rest" mass is $6.0 \times 10^{24}\text{ kg}$.

- (a) What is the kinetic energy of the earth in its orbit?
- (b) What is the mass equivalent of that kinetic energy?
- (c) By what percentage is the earth's "rest" mass increased at orbital speed?
- (d) Refer back to Unit 2 to recall how the mass of the earth is found; was it the rest mass or the mass at orbital speed?

20.7 In relativistic mechanics the formula $\vec{p} = m\vec{v}$ still holds, but the mass m is given by $m = m_0/\sqrt{1 - v^2/c^2}$. The rest mass of an electron is $9.1 \times 10^{-31}\text{ kg}$.

- (a) What is its momentum when it is moving down the axis of a linear accelerator from left to right at a speed of $0.4c$ with respect to the accelerator tube?
- (b) What would Newton have calculated for the momentum of the electron?
- (c) By how much would the relativistic momentum increase if the speed of the electron were doubled?
- (d) What would Newton have calculated its change in momentum to be?

20.8 Calculate the momentum of a photon of wavelength 4000 Å . How fast would an electron have to move in order to have the same momentum?

20.9 Construct a diagram showing the change that occurs in the frequency of a photon as a result of its collision with an electron.

20.10 What explanation would you offer for the fact that the wave aspect of light was shown to be valid before the particle aspect was demonstrated?

20.11 The electrons which produced the diffraction photograph on p. 102 had de Broglie wavelengths of 10^{-10} meter. To what speed must they have been accelerated? (Assume that the

speed is small compared to c , so that the electron mass is about 10^{-30} kg.)

20.12 A billiard ball of mass 0.2 kilograms moves with a speed of 1 meter per second. What is its de Broglie wavelength?

20.13 Show that the de Broglie wavelength of a classical particle of mass m and kinetic energy KE is given by

$$\lambda = \frac{h}{\sqrt{2m(KE)}}$$

What happens when the mass is very small and the speed is very great?

20.14 A particle confined in a box cannot have a kinetic energy less than a certain amount; this least amount corresponds to the longest de Broglie wavelength which produces standing waves in the box; that is, the box size is one-half wavelength. For each of the following situations find the longest de Broglie wavelength that would fit in the box: then use $p = h/\lambda$ to find the momentum p , and use $p = mv$ to find the speed v .

- (a) a dust particle (about 10^{-9} kg) in a display case (about 1 m across).
- (b) an argon atom (6.6×10^{-26} kg) in a light bulb (about 10^{-1} m across).
- (c) a protein molecule (about 10^{-22} kg) in a bacterium (about 10^{-6} m across).
- (d) an electron (about 10^{-30} kg) in an atom (about 10^{-10} m across).

20.15 Suppose that the only way you could obtain information about the world was by throwing rubber balls at the objects around you and measuring their speeds and directions of rebound. What kind of objects would you be unable to learn about?

20.16 A bullet can be considered as a particle having dimensions approximately 1 centimeter. It has a mass of about 10 grams and a speed of about 3×10^4 centimeters per second. Suppose we can measure its speed to an accuracy of ± 1 cm/sec. What is the corresponding uncertainty in its position according to Heisenberg's principle?

20.17 Show that if Planck's constant were equal to zero, quantum effects would disappear and even atomic particles would behave according to Newtonian physics. What effect would this have on the properties of light?

20.18 Some writers have claimed that the uncertainty principle proves that there is free will. Do you think this extrapolation from atomic phenomena to the world of animate beings is justified?

20.19 A physicist has written

It is enough that quantum mechanics predicts the average value of observable quantities correctly. It is not really essential that the mathematical symbols and processes correspond to some intelligible physical picture of the atomic world.

Do you regard such a statement as acceptable? Give reasons.

20.20 In Chapters 19 and 20 we have seen that it is impossible to avoid the wave-particle dualism of light and matter. Bohr has coined the word *complementarity* for the situation in which two opposite views seem valid, and the correct choice depends only on which aspect of a phenomenon one chooses to consider. Can you think of situations in other fields (outside of atomic physics) to which this idea might apply?

20.21 In Units 1 through 4 we discussed the behavior of large-scale "classical particles" (for example, tennis balls) and "classical waves" (for example, sound waves), that is, of particles and waves that in most cases can be described without any use of ideas such as the quantum of energy or the de Broglie matter-wave. Does this mean that there is one sort of physics ("classical physics") for the phenomena of the large-scale world and quite a different physics ("quantum physics") for the phenomena of the atomic world? Or does it mean that quantum physics really applies to all phenomena but is not distinguishable from classical physics when applied to large-scale particles and waves? What arguments or examples would you use to defend your answer?

20.22 If there are laws that describe precisely the behavior of atoms, it can be inferred that the future is completely determined by the present (and the present was determined in the ancient past). This idea of complete *determinism* was uncomfortable to many philosophers during the centuries following the great success of Newtonian mechanics. The great French physicist Pierre Laplace (1748-1827) wrote,

Given for one instant an intelligence which could comprehend all the forces by which nature is animated and the respective situation of the beings who compose it—an intelligence sufficiently vast to submit these data to analysis—it would embrace in the same formula the movements of the greatest bodies of the universe and those of the lightest atom; for it, nothing would be uncertain and the future, as the past, would be present to its eyes [*A Philosophical Essay on Probabilities*.]

Is this statement consistent with modern physical theory?

20.23 (The later statistical view of kinetic theory may have emphasized the difficulty of actually predicting the future, but did not weaken the idea of an underlying chain of cause and effect.)

- (a) What implications do you see in relativity theory for the idea of determinism?

- (b) What implications do you see for determinism in quantum theory?

20.24 Those ancient Greeks who believed in natural law were also troubled by the idea of determinism. How do the Greek ideas expressed in the following passage from Lucretius' *On the Nature of Things* (about 80 B.C.) compare with modern physics ideas?

If cause forever follows after cause
In infinite, undeviating sequence
And a new motion always has to come
Out of an old one, by fixed law; if atoms

Do not, by swerving, cause new moves which break

The laws of fate; if cause forever follows,
In infinite sequence, cause—where would we get

This free will that we have, wrested from fate . . .
What keeps the mind from having inside itself
Some such compulsiveness in all its doings,
What keeps it from being matter's absolute slave?

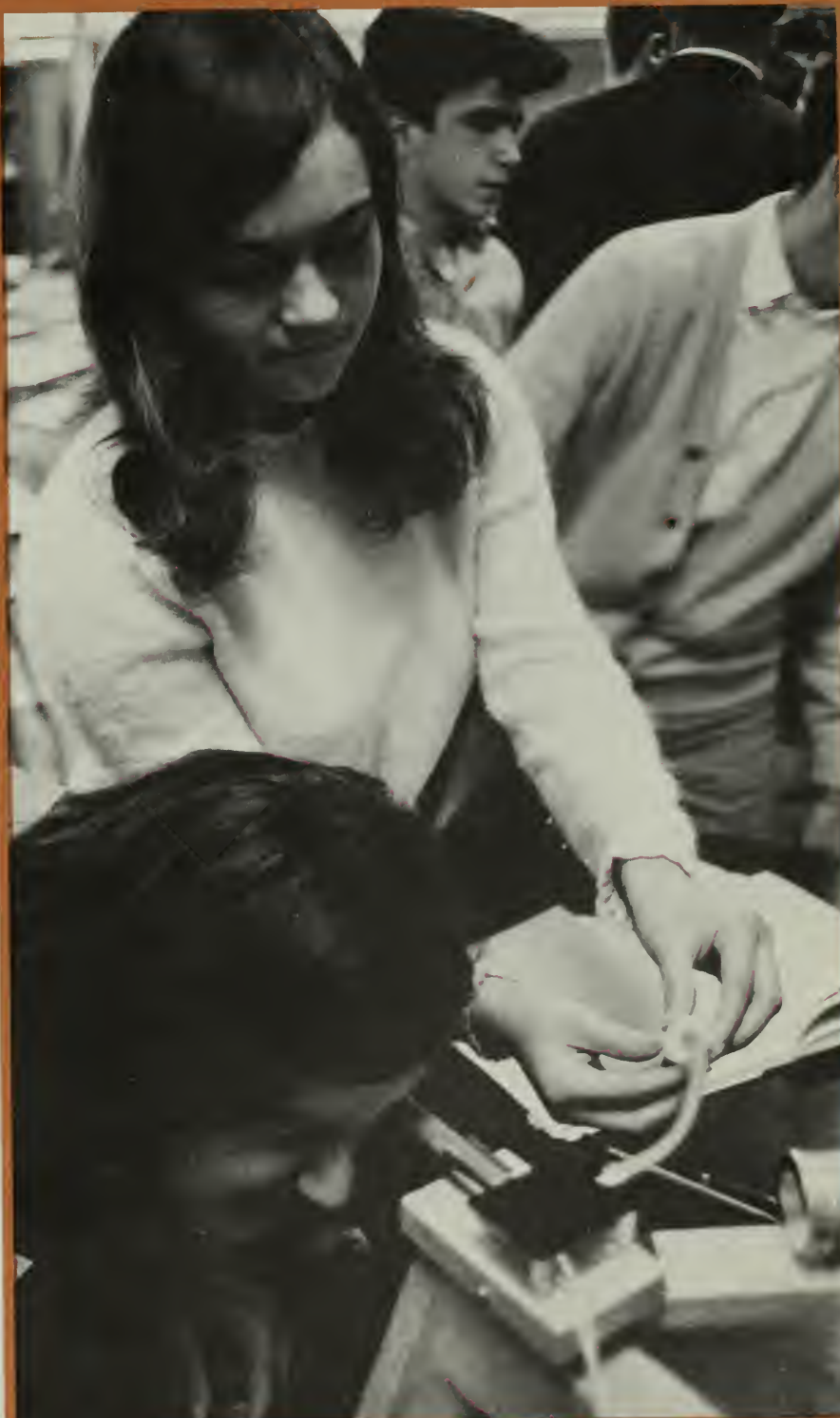
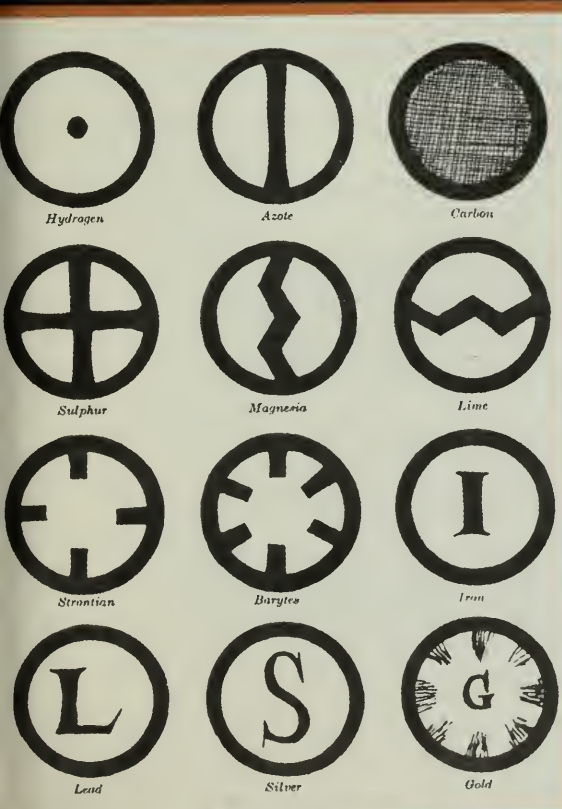
The answer is that our free-will derives
From just that ever-so-slight atomic swerve
At no fixed time, at no fixed place whatever.

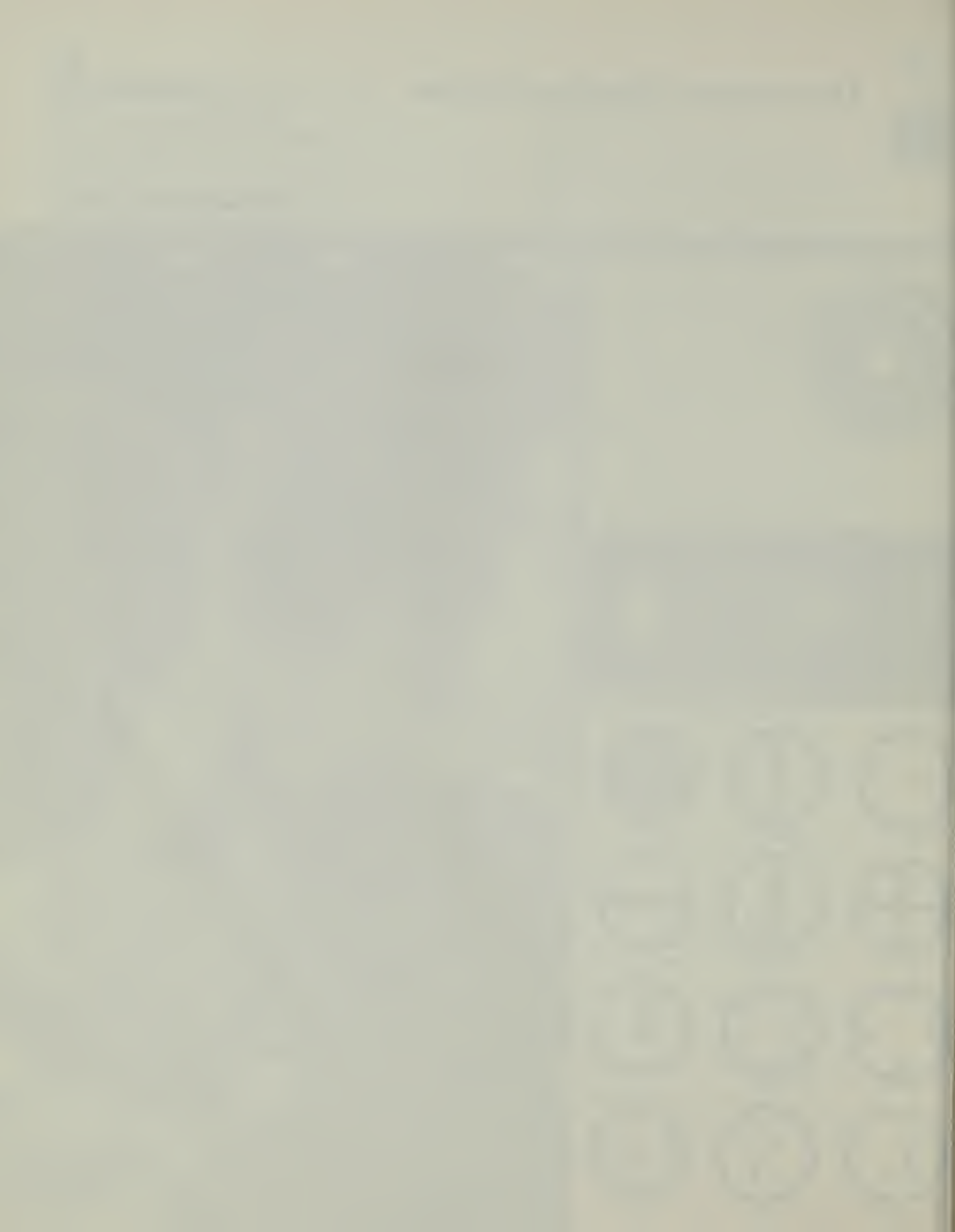
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Models of the Atom





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Chapter 17 The Chemical Basis of Atomic Theory

EXPERIMENT 40 ELECTROLYSIS

Volta and Davy discovered that electric currents created chemical changes never observed before. As you have already learned, these scientists were the first to use electricity to break down apparently stable compounds and to isolate certain chemical elements.

Later Faraday and other experimenters compared the *amount* of electric charge used with the *amount* of chemical products formed in such electrochemical reactions. Their measurements fell into a regular pattern that hinted at some underlying link between electricity and matter.

In this experiment you will use an electric current just as they did to decompose a compound. By comparing the charge used with the mass of one of the products, you can compute the mass and volume of a single atom of the product.

Theory Behind the Experiment

A beaker of copper sulfate (CuSO_4) solution in water is supported under one arm of a balance (Fig. 17-1). A negatively charged copper electrode is supported in the solution by the bal-

ance arm so that you can measure its mass without removing it from the solution. A second, positively charged copper electrode fits around the inside wall of the beaker. The beaker, its solution and the positive electrode are *not* supported by the balance arm.

If you have studied chemistry, you probably know that in solution the copper sulfate comes apart into separate charged particles, called ions, of copper (Cu^{++}) and sulfate (SO_4^{--}), which move about freely in the solution.

When a voltage is applied across the copper electrodes, the electric field causes the SO_4^{--} ions to drift to the positive electrode (or anode) and the Cu^{++} ions to drift to the negative electrode (or cathode). At the cathode the Cu^{++} particles acquire enough negative charge to form neutral copper atoms which deposit on the cathode and add to its weight. The motion of charged particles toward the electrodes is a continuation of the electric current in the wires and the rate of transfer of charge (coulombs per second) is equal to it in magnitude. The electric current is provided by a power supply that converts 100-volt alternating current into low-voltage direct current. The current

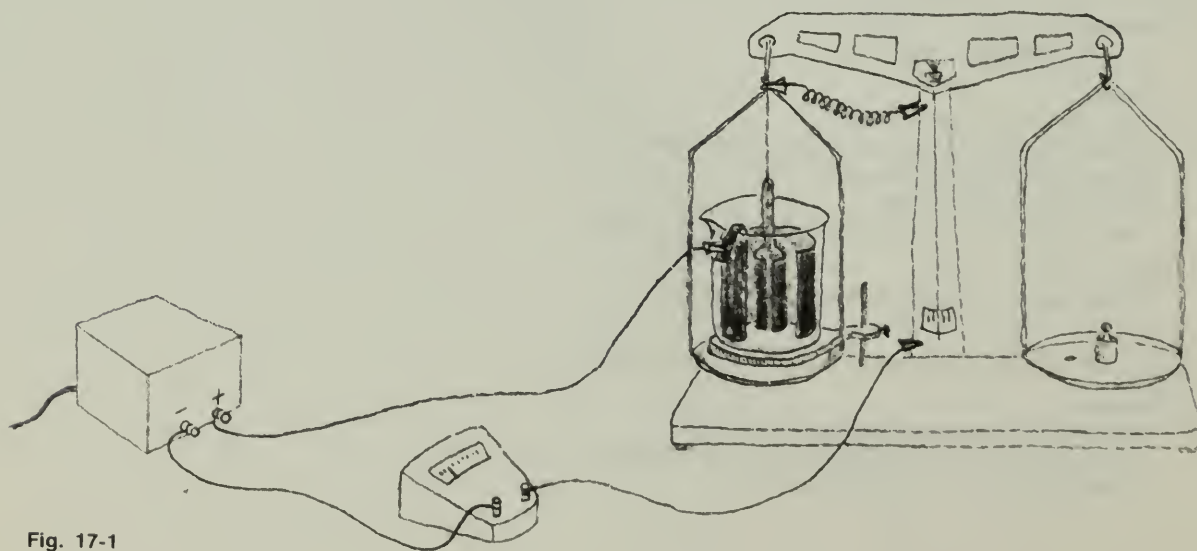


Fig. 17-1

is set by a variable control on the power supply (or by an external rheostat) and measured by an ammeter in series with the electrolytic cell as shown in Fig. 17-1.

With the help of a watch to measure the time the current flows, you can compute the electric charge that passed through the cell. By definition, the current I is the rate of transfer or charge: $I = \Delta Q / \Delta t$. It follows that the charge transferred is the product of the current and the time.

$$\Delta Q = I \times \Delta t$$

$$(\text{coulombs} = \frac{\text{coulombs}}{\text{sec}} \times \text{sec})$$

Since the amount of charge carried by a single electron is known ($q_e = 1.6 \times 10^{-19}$ coulombs), the number of electrons transferred, N_e , is

$$N_e = \frac{\Delta Q}{q_e}$$

If n electrons are needed to neutralize each copper ion, then the number of copper atoms deposited, N_{Cu} , is

$$N_{Cu} = \frac{N_e}{n}$$

If the mass of each copper atom is m_{Cu} , then the total mass of copper deposited, M_{Cu} , is

$$M_{Cu} = N_{Cu} m_{Cu}$$

Thus, if you measure I , Δt and M_{Cu} , and you know q_e and n , you can calculate a value for m_{Cu} , the mass of a single copper atom!

Setup and Procedure

Either an equal-arm or a triple-beam balance can be used for this experiment. First arrange the cell and the balance as shown in Fig. 17-1. The cathode cylinder must be supported far enough above the bottom of the beaker so that the balance arm can move up and down freely when the cell is full of the copper sulfate solution.

Next connect the circuit as illustrated in

the figure. Note that the electrical connection from the negative terminal of the power supply to the cathode is made through the balance beam. The knife-edge and its seat *must* be bypassed by a short piece of thin flexible wire, as shown in Fig. 17-1 for equal-arm balances, or in Fig. 17-2 for triple-beam balances. The positive terminal of the power supply is connected directly to the anode in any convenient manner.

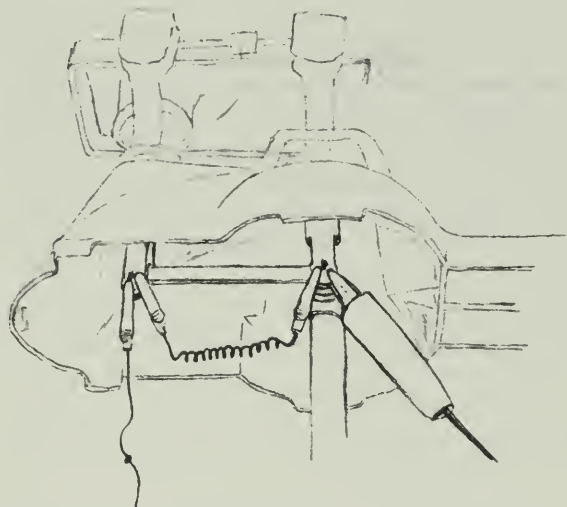


Fig. 17-2 This cutaway view shows how to by-pass the knife-edge of a typical balance. The structure of other balances may differ.

Before any measurements are made, operate the cell long enough (10 or 15 minutes) to form a preliminary deposit on the cathode—unless this has already been done. In any case, run the current long enough to set it at the value recommended by your teacher, probably about 5 amperes.

When all is ready, adjust the balance and record its reading. Pass the current for the length of time recommended by your teacher. Measure and record the current I and the time interval Δt during which the current passes. Check the ammeter occasionally and, if necessary, adjust the control in order to keep the current set at its original value.

At the end of the run, record the new reading of the balance, and find by subtraction the increase in mass of the cathode.

Calculating Mass and Volume of an Atom

Since the cathode is buoyed up by a liquid, the masses you have measured are not the true masses. Because of the buoyant force exerted by the liquid, the mass of the cathode and its increase in mass will both appear to be less than they would be in air. To find the true mass increase, you must divide the observed mass increase by the factor $(1 - D_s/D_c)$, where D_s is the density of the solution and D_c is the density of the copper.

Your teacher will give you the values of these two densities if you cannot find values for them yourself. He will also explain how the correction factor is derived. The important thing for you to understand here is why a correction factor is necessary.

Q1 How much positive or negative charge was transferred to the cathode?

In the solution this positive charge is carried from anode to cathode by doubly charged copper ions, Cu^{++} . At the cathode the copper ions are neutralized by electrons and neutral copper atoms are deposited: $\text{Cu}^{++} + 2\text{e}^- \rightarrow \text{Cu}$.

Q2 How many electrons were required to neutralize the total charge transferred? (Each electron carries -1.6×10^{-19} coulombs.)

Q3 How many electrons (single negative charge) were required to neutralize each copper ion?

Q4 How many copper atoms were deposited?

Q5 What is the mass of each copper atom?

Q6 The mass of a penny is about 3 grams. If it were made of copper only, how many atoms would it contain? (In fact modern pennies contain zinc as well as copper.)

Q7 The volume of a penny is about 0.3 cm^3 . How much volume does each atom occupy?

ACTIVITIES

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DALTON'S PUZZLE

Once Dalton had his theory to work with, the job of figuring out relative atomic masses and empirical formulas boiled down to nothing more than working through a series of puzzles. Here is a very similar kind of puzzle with which you can challenge your classmates.

Choose three sets of objects, each having a different mass. Large ball bearing with masses of about 70, 160, and 200 grams work well. Let the smallest one represent an atom of hydrogen, the middle-sized one an atom of nitrogen, and the large one an atom of oxygen.

From these "atoms" construct various "molecules." For example, NH_3 could be represented by three small objects and one middle-sized one, N_2O by two middle-sized ones and one large, and so forth.

Conceal one molecule of your collection in each one of a series of covered Styrofoam cups (or other light-weight, opaque containers). Mark on each container the symbols (but not the formula!) of the elements contained in the compound. Dalton would have obtained this information by qualitative analysis.

Give the covered cups to other students. Instruct them to measure the "molecular" mass of each compound and to deduce the relative atomic masses and empirical formulas from the set of masses, making Dalton's assumption of simplicity. If the objects you have used for "atoms" are so light that the mass of the styrofoam cups must be taken into account, you can either supply this information as part of the data or leave it as a complication in the problem.

If the assumption of simplicity is relaxed, what other atomic masses and molecular formulas would be consistent with the data?

ELECTROLYSIS OF WATER

The fact that electricity can decompose water was an amazing and exciting discovery, yet the process is one that you can easily demonstrate with materials at your disposal. Fig. 17-3 provides all the necessary information. Set up an electrolysis apparatus and demonstrate the process for your classmates.

In Fig. 17-3 it looks as if about twice as

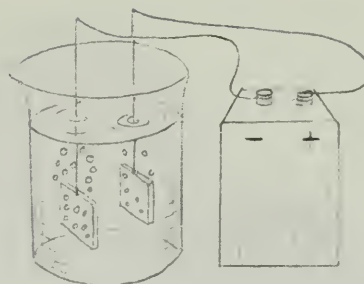


Fig. 17-3

many bubbles were coming from one electrode as from the other. Which electrode is it? Does this happen in your apparatus? Would you expect it to happen?

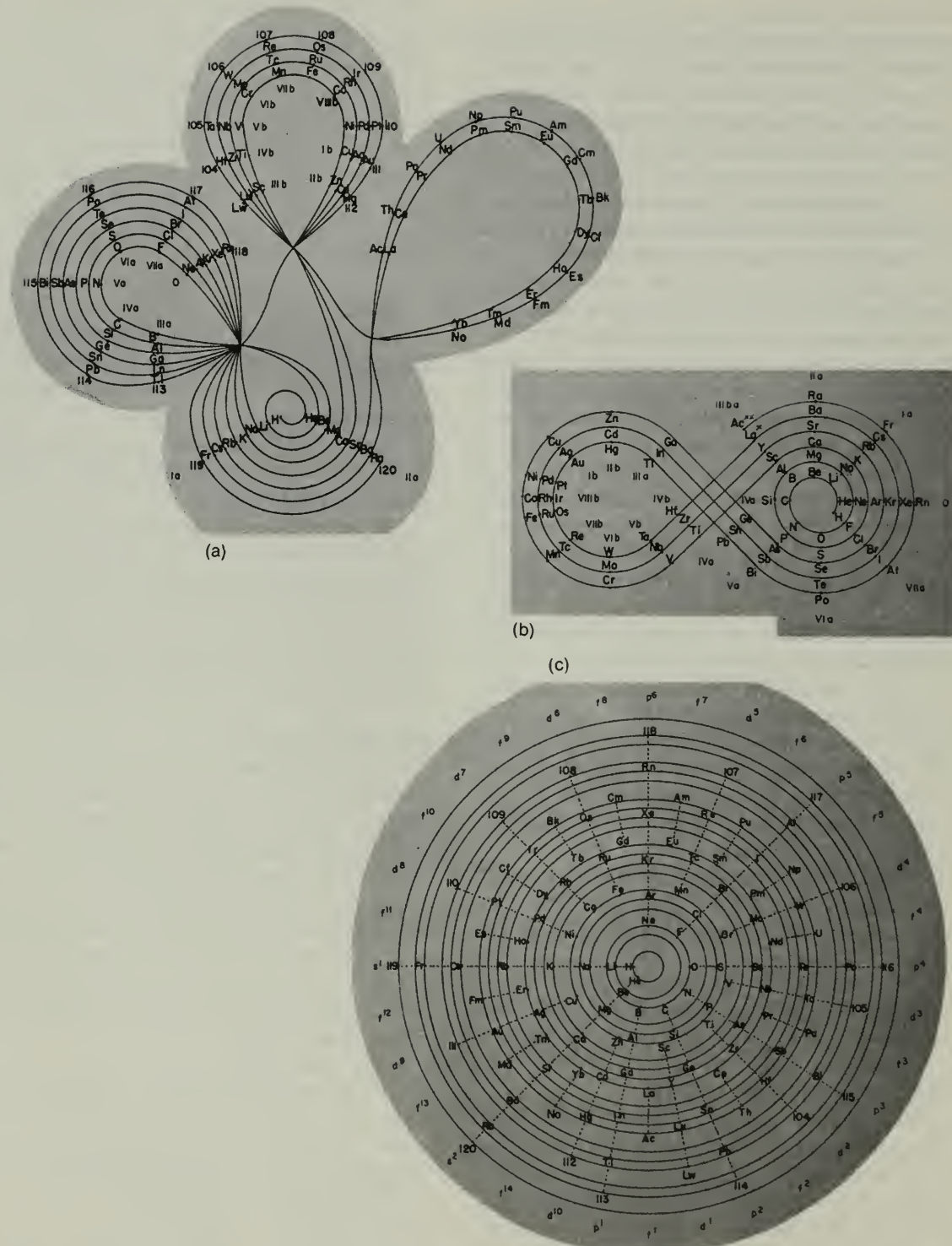
How would you collect the two gases that bubble off the electrodes? How could you prove their identity?

If water is really just these two gases "put together" chemically, you should be able to put the gases together again and get back the water with which you started. Using your knowledge of physics, predict what must then happen to all the electrical energy you sent flowing through the water to separate it.

PERIODIC TABLE

You may have seen one or two forms of the periodic table in your classroom, but many others have been devised to emphasize various relationships among the elements. Some, such as the ones shown on the next page, are more visually interesting than others. Check various sources in your library and prepare an exhibit of the various types. An especially good lead is the article, "Ups and Down of the Periodic Table" in *Chemistry*, July 1966, which shows many different forms of the table, including those in Fig. 17-4.

It is also interesting to arrange the elements in order of discovery on a linear time chart. Periods of intense activity caused by breakthroughs in methods of extended work by a certain group of investigators show up in groups of names. A simple way to do this is to use a typewriter, letting each line represent one year (from 1600 on). All the elements then fit on six normal typing pages which can be



Three two-dimensional spiral forms. (a) Janet, 1928. (b) Kipp, 1942. (c) Sibaiua, 1941.

fastened together for mounting on a wall. A list of discovery dates for all elements appears at the end of Chapter 21 in the Text.

SINGLE-ELECTRODE PLATING

A student asked if copper would plate out from a solution of copper sulfate if only a negative electrode were placed in the solution. It was tried and no copper was observed even when the electrode was connected to the negative terminal of a high voltage source for five minutes. Another student suggested that only a very small (invisible) amount of copper was deposited since copper ions should be attracted to a negative electrode.

A more precise test was devised. A nickel-sulfate solution was made containing several microcuries of radioactive nickel (no radio-copper was available). A single carbon electrode was immersed in the solution, and connected to the negative terminal of the high voltage source again for five minutes. The electrode was removed, dried, and tested with a Geiger counter. The rod was slightly radioactive. A control test was run using identical test conditions, except that *no* electrical connection was made to the electrode. The control showed *more* radioactivity.

Repeat these experiments and see if the effect is true generally. What explanation would you give for these effects? (Adapted

from *Ideas for Science Investigations*, N. S.-T. A. 1966).

ACTIVITIES FROM SCIENTIFIC AMERICAN

The following articles from the "Amateur Scientist" section of *Scientific American* relate to Unit 5. They range widely in difficulty.

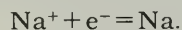
- Accelerator, electron, Jan. 1959, p. 138.
- Beta ray spectrometer, Sept. 1958, p. 197.
- Carbon 14 dating, Feb. 1957, p. 159.
- Cloud chamber, diffusion, Sept. 1952, p. 179.
- Cloud chamber, plumber's friend, Dec. 1956, p. 169.
- Cloud chamber, Wilson, Apr. 1956, p. 156.
- Cloud chamber, with magnet, June 1959, p. 173.
- Cyclotron, Sept. 1953, p. 154.
- Gas discharge tubes, how to make, Feb. 1958, p. 112.
- Geiger counter, how to make, May 1960, p. 189.
- Isotope experiments, May 1960, p. 189.
- Magnetic resonance spectrometer, Apr. 1959, p. 171.
- Scintillation counter, Mar. 1953, p. 104.
- Spectrograph, astronomical, Sept. 1956, p. 259.
- Spectrograph, Bunsen's, June 1955, p. 122.
- Spinthariscopes, Mar. 1953, p. 104.
- Spectroheliograph, how to make, Apr. 1958, p. 126.
- Subatomic particle scattering, simulating, Aug. 1965, p. 102.

FILM LOOP

FILM LOOP 46: PRODUCTION OF SODIUM BY ELECTROLYSIS

In 1807, Humphry Davy produced metallic sodium by electrolysis of molten lye—sodium hydroxide.

In the film, sodium hydroxide (NaOH) is placed in an iron crucible and heated until it melts, at a temperature of 318°C. A rectifier connected to a power transformer supplies a steady current through the liquid NaOH through iron rods inserted in the melt. Sodium ions are positive and are therefore attracted to the negative electrode; there they pick up electrons and become metallic sodium, as indicated symbolically in this reaction:



The sodium accumulates in a thin, shiny layer floating on the surface of the molten sodium hydroxide.

Sodium is a dangerous material which combines explosively with water. The experimenter in the film scoops out a little of the metal and places it in water. (Fig. 17-5.) Energy is released rapidly, as you can see from the violence of the reaction. Some of the sodium is vaporized and the hot vapor emits the yellow light characteristic of the spectrum of sodium. The same yellow emission is easily seen if common salt, sodium chloride, or some other sodium compound, is sprinkled into an open flame.



Fig. 17-5

Chapter 18 Electrons and Quanta

EXPERIMENT 41 THE CHARGE-TO-MASS RATIO FOR AN ELECTRON

In this experiment you make measurements on cathode rays. A set of similar experiments by J. J. Thomson convinced physicists that these rays are not waves but streams of identical charged particles, each with the same ratio of charge to mass. If you did experiment 38 in Unit 4, "Electron-Beam Tube," you have already worked with cathode rays and have seen how they can be deflected by electric and magnetic fields.

Thomson's use of this deflection is described on page 36 of the Unit 5 *Text*. Read that section of the text before beginning this experiment.

Theory of the experiment

The basic plan of the experiment is to measure the bending of the electron beam by a known magnetic field. From these measurements and a knowledge of the voltage accelerating the electrons, you can calculate the electron charge-to-mass ratio. The reasoning behind the calculation is illustrated in Fig. 18-1. The algebraic steps are described below.

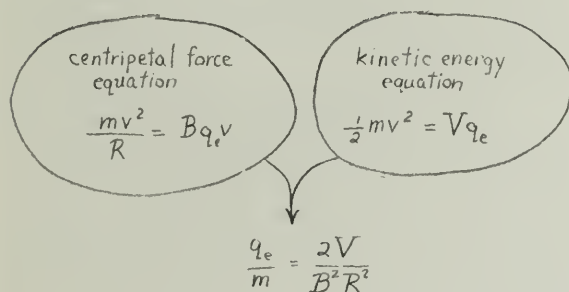


Fig. 18-1 The combination of two relationships, for centripetal and kinetic energy, with algebraic steps that eliminate velocity, v , lead to an equation for the charge-to-mass ratio of an electron.

When the beam of electrons (each of mass m and charge q_e) is bent into a circular arc of

radius R by a uniform magnetic field B , the centripetal force mv^2/R on each electron is supplied by the magnetic force $Bq_e v$. Therefore

$$\frac{mv^2}{R} = Bq_e v,$$

or, rearranging to get v by itself,

$$v = \frac{Bq_e r}{m}.$$

The electrons in the beam are accelerated by a voltage V which gives them a kinetic energy

$$\frac{mv^2}{2} = Vq_e.$$

If you replace v in this equation by the expression for v in the preceding equation, you get

$$\frac{m}{2} = \left(\frac{Bq_e R}{m} \right)^2 = Vq_e$$

or, after simplifying,

$$\frac{q_e}{m} = \frac{2V}{B^2 R^2}.$$

You can measure with your apparatus all the quantities on the right-hand side of this expression, so you can use it to calculate the charge-to-mass ratio for an electron.

Preparing the apparatus

You will need a tube that gives a beam at least 5 cm long. If you kept the tube you made in Experiment 38, you may be able to use that. If your class didn't have success with this experiment, it may mean that your vacuum pump is not working well enough, in which case you will have to use another method.

In this experiment you need to be able to adjust the strength of the magnetic field until the magnetic force on the charges just balances the force due to the electric field. To enable you to change the magnetic field, you will use a pair of coils instead of permanent magnets. A current in a pair of coils, which are separated by a distance equal to the coil radius, produces a nearly uniform magnetic field in the central region between the coils. You can vary the magnetic field by changing the current in the coils.

Into a cardboard tube about 3" in diameter and 3" long cut a slot $1\frac{1}{4}$ " wide. (Fig. 18-2.) Your electron-beam tube should fit into this slot as shown in the photograph of the completed set-up. (Fig. 18-4.) Current in the pair of coils will create a magnetic field at right angles to the axis of the cathode rays.

Now wind the coils, one on each side of the slot, using a single length of insulated copper wire (magnet wire). Wind about 20 turns of wire for each of the two coils, one coil on each side of the slot, leaving 10" of wire free at both ends of the coil. Don't cut the wire off the reel until you have found how much you will need. Make the coils as neat as you can and keep them close to the slot. Wind both coils in the same sense (for example, make both clockwise).

When you have made your set of coils, you must "calibrate" it; that is, you must find out what magnetic field strength B corresponds to what values of current I in the coils. To do

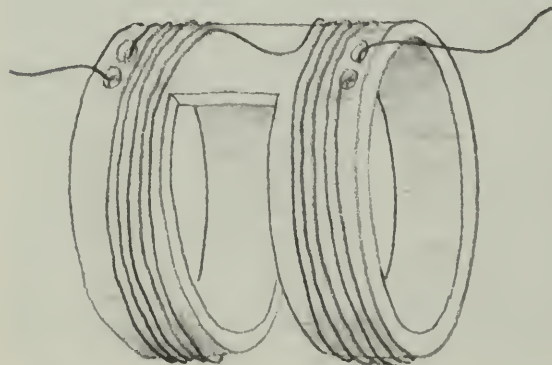


Fig. 18-2

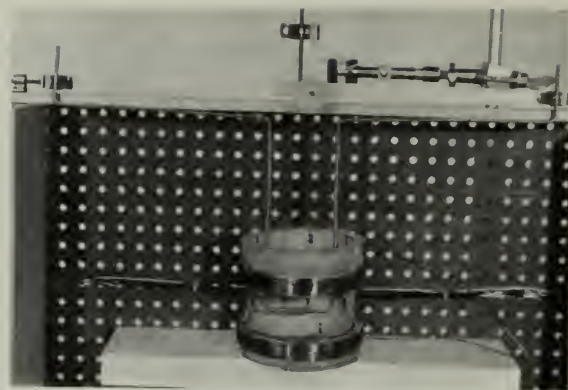


Fig. 18-3

this, you can use the current balance, as you did in Experiment 36. Use the shortest of the balance "loops" so that it will fit inside the coils as shown in Fig. 18-3.

Connect the two leads from your coils to a power supply capable of giving up to 5 amps direct current. There must be a variable control on the power supply (or a rheostat in the circuit) to control the current; and an ammeter to measure it.

Measure the force F for a current I in the loop. To calculate the magnetic field due to the current in the coils, use the relationship $F = BIl$ where l is the length of short section of the loop. Do this for several different values of current in the coil and plot a calibration graph of magnetic field B against coil current I .

Set up your electron-beam tube as in Experiment 38. Reread the instructions for operating the tube.

Connect a shorting wire between the pins for the deflecting plates. This will insure that the two plates are at the same electric potential, so the electric field between them will be zero. Pump the tube out and adjust the filament current until you have an easily visible beam. Since there is no field between the plates, the electron beam should go straight up the center of the tube between the two plates. (If it does not, it is probably because the filament and the hole in the anode are not properly aligned.)

Turn down the filament current and switch off the power supply. Now, without releasing



Fig. 18-4 The magnetic field is parallel to the axis of the coils; the electric and magnetic fields are perpendicular to each other and to the electron beam.

the vacuum, mount the coils around the tube as shown in Fig. 18-4.

Connect the coils as before to the power supply. Connect a voltmeter across the power supply terminals that provide the accelerating voltage V .

Your apparatus is now complete.

Performing the experiment

Turn on the beam, and make sure it is traveling in a straight line. The electric field remains off throughout the experiment, and the deflecting plates should still be connected together.

Turn on and slowly increase the current in the coils until the magnetic field is strong enough to deflect the electron beam noticeably.

Record the current I in the coils.

Using the calibration graph, find the magnetic field B .

Record the accelerating voltage V between the filament and the anode plate.

Finally you need to measure R , the radius of the arc into which the beam is bent by the magnetic field. The deflected beam is slightly fan-shaped because some electrons are slowed by collisions with air molecules and are bent into a curve of smaller R . You need to know the largest value of R (the "outside" edge of the curved beam), which is the path of electrons that have made no collisions. You won't be able to measure R directly, but you can find

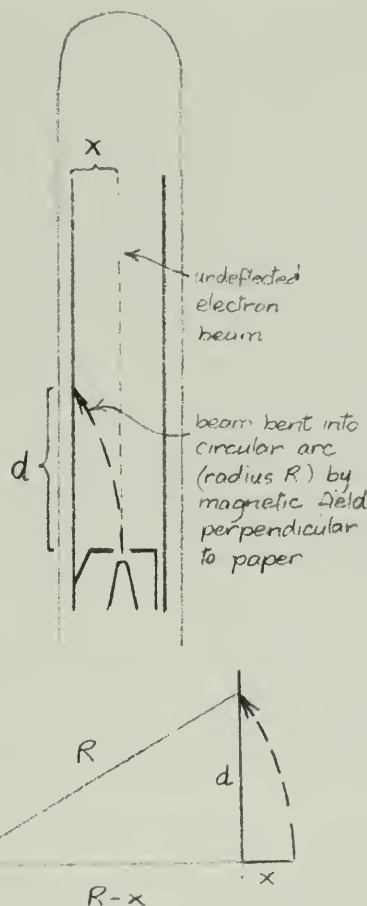


Fig. 18-5

it from measurements that are easy to make. (Fig. 18-5.)

You can measure x and d . It follows from Pythagoras' theorem that $R^2 = d^2 + (R - x)^2$,

$$\text{so } R = \frac{d^2 + x^2}{2x}.$$

Q1 What is your calculation of R on the basis of your measurements?

Now that you have values for V , B and R , you can use the formula $q_e/m = 2V/B^2R^2$ to calculate your value for the charge-to-mass ratio for an electron.

Q2 What is your value for q_e/m , the charge-to-mass ratio for an electron?

EXPERIMENT 42 THE MEASUREMENT OF ELEMENTARY CHARGE

In this experiment, you will investigate the charge of the electron, a fundamental physical constant in electricity, electromagnetism, and nuclear physics. This experiment is substantially the same as Millikan's famous oil-drop experiment, described on page 39 of the Unit 5 Text. The following instructions assume that you have read that description. Like Millikan, you are going to measure very small electric charges to see if there is a limit to how small an electric charge can be. Try to answer the following three questions before you begin to do the experiment in the lab.

Q1 What is the electric field between two parallel plates separated by a distance d meters, if the potential difference between them is V volts?

Q2 What is the electric force on a particle carrying a charge of q coulombs in an electric field of E volts/meter?

Q3 What is the gravitational force on a particle of mass m in the earth's gravitational field?

Background

Electric charges are measured by measuring the forces they experience and produce. The extremely small charges that you are seeking require that you measure extremely small forces. Objects on which such small forces can have a visible effect must also in turn be very small.

Millikan used the electrically charged droplets produced in a fine spray of oil. The varying size of the droplets complicated his measurements. Fortunately you can now use suitable objects whose sizes are accurately known. You use tiny latex spheres (about 10^{-4} cm diameter), which are almost identical in size in any given sample. In fact, these spheres, shown magnified (about 5000 \times) in Fig. 18-6, are used as a convenient way to find the magnifying power of electron microscopes. The spheres can be bought in a water suspension, with their diameter recorded on the bottle. When the suspension is sprayed into the air, the water quickly evaporates and leaves

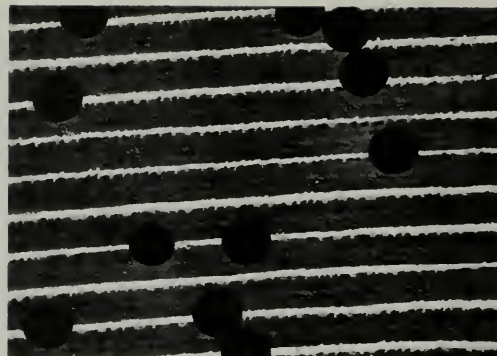


Fig. 18-6 Electron micrograph of latex spheres 1.1×10^{-4} cm, silhouetted against diffracting grating of 28,800 lines/inch. What magnification does this represent?

a cloud of these particles, which have become charged by friction during the spraying. In the space between the plates of the Millikan apparatus they appear through the 50-power microscope as bright points of light against a dark background.

You will find that an electric field between the plates can pull some of the particles upward against the force of gravity, so you will know that they are charged electrically.

In your experiment, you adjust the voltage producing the electric field until a particle hangs motionless. On a balanced particle carrying a charge q , the upward electric force Eq and the downward gravitational force ma_g are equal, so

$$ma_g = Eq.$$

The field $E = V/d$, where V is the voltage between the plates (the voltmeter reading) and d is the separation of the plates. Hence

$$q = \frac{ma_g d}{V}.$$

Notice that $ma_g d$ is a constant for all measurements and need be found only once. Each value of q will be this constant $ma_g d$ times $1/V$ as the equation above shows. That is, the value of q for a particle is proportional to $1/V$: the greater the voltage required to balance the weight of the particle, the smaller the charge of the particle must be.

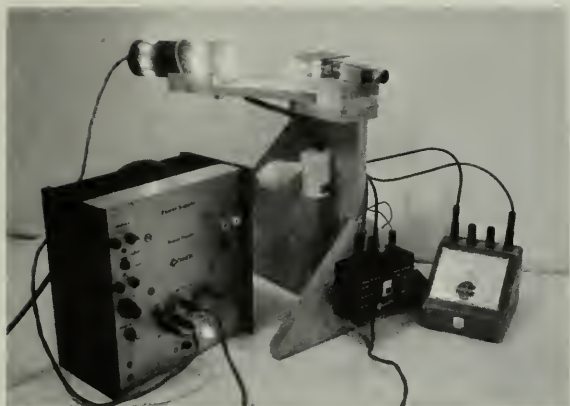


Fig. 18-7 A typical set of apparatus. Details may vary considerably.

Using the apparatus

If the apparatus is not already in operating condition, consult your teacher. Study Figs. 18-7 and 18-8 until you can identify the various parts. Then switch on the light source and look through the microscope. You should see a series of lines in clear focus against a uniform gray background.

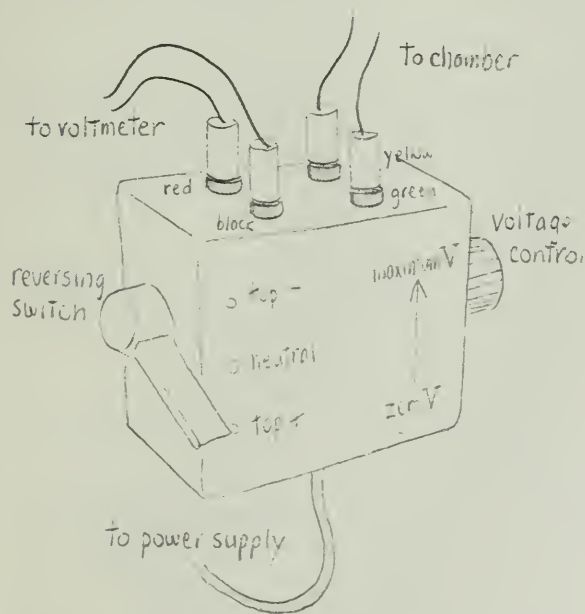


Fig. 18-8 A typical arrangement of connections to the high-voltage reversing switch.

The lens of the light source may fog up as the heat from the lamp drives moisture out of

the light-source tube. If this happens, remove the lens and wipe it on a clean tissue. Wait for the tube to warm up thoroughly before replacing the lens.

Squeeze the bottle of latex suspension two or three times until five or ten particles drift into view. You will see them as tiny bright spots of light. You may have to adjust the focus slightly to see a specific particle clearly. Notice how the particle appears to move upward. The view is inverted by the microscope—the particles are actually falling in the earth's gravitational field.

Now switch on the high voltage across the plates by turning the switch up or down. Notice the effect on the particles of varying the electric field by means of the voltage-control knob.

Notice the effect when you reverse the electric field by reversing the switch position. (When the switch is in its mid-position, there is zero field between the plates.)

Q4 Do all the particles move in the same direction when the field is on?

Q5 How do you explain this?

Q6 Some particles move much more rapidly in the field than others. Do the rapidly moving particles have larger or smaller charges than the slowly moving particles?

Sometimes a few particles cling together, making a clump that is easy to see—the clump falls more rapidly than single particles when the electric field is off. Do not try to use these for measuring q .

Try to balance a particle by adjusting the field until the particle hangs motionless. Observe it carefully to make sure it isn't slowly drifting up or down. The smaller the charge, the greater the electric field must be to hold up the particle.

Taking data

It is not worth working at voltages much below 50 volts. Only highly charged particles can be balanced in these small fields, and you are interested in obtaining the smallest charge possible.

Set the potential difference between the plates to about 75 volts. Reverse the field a

few times so that the more quickly moving particles (those with greater charge) are swept out of the field of view. Any particles that remain have low charges. If *no* particles remain, squeeze in some more and look again for some with small charge.

When you have isolated one of these particles carrying a low charge, adjust the voltage carefully until the particle hangs motionless. Observe it for some time to make sure that it isn't moving up or down very slowly, and that the adjustment of voltage is as precise as possible. (Because of uneven bombardment by air molecules, there will be some slight, uneven drift of the particles.)

Read the voltmeter. Then estimate the precision of the voltage setting by seeing how little the voltage needs to be changed to cause the particle to start moving just perceptibly. This small change in voltage is the greatest amount by which your *setting* of the balancing voltage can be uncertain.

When you have balanced a particle, make sure that the voltage setting is as precise as you can make it before you go on to another particle. The most useful range to work in is 75–150 volts, but try to find particles that can be brought to rest in the 200–250 volt range too, if the meter can be used in that range. Remember that the higher the balancing field the smaller the charge on the particle.

In this kind of an experiment, it is helpful to have large amounts of data. This usually makes it easier to spot trends and to distinguish main effects from the background scattering of data. Thus you may wish to contribute your findings to a class data pool. Before doing that, however, arrange your values of V in a vertical column of increasing magnitude.

Q7 Do the numbers seem to clump together in groups, or do they spread out more or less evenly from the lowest to the highest values?

Now combine your data with that collected by your classmates. This can conveniently be done by placing your values of V on a class histogram. When the histogram is complete, the results can easily be transferred to a transparent sheet for use on an overhead projector. Alternatively, you may wish to take a Polaroid

photograph of the completed histogram for inclusion in your laboratory notebook.

Q8 Does your histogram suggest that all values of q are possible and that electric charge is therefore endlessly divisible, or the converse?

If you would like to make a more complete quantitative analysis of the class results, calculate an average value for each of the highest three or four clumps of V values in the class histogram. Next change those to values of $1/V$ and list them in order. Since q is proportional to $1/V$, these values represent the magnitude of the charges on the particles.

To obtain actual values for the charges, the $1/V$'s must be multiplied by $ma_g d$. The separation d of the two plates, typically about 5.0 mm, or 5.0×10^{-3} m, is given in the specification sheets provided by the manufacturer. You should check this.

The mass m of the spheres is worked out from a knowledge of their volume and the density D of the material they are made from.

Mass = volume \times density, or

$$m = \frac{4}{3} r^3 \times D$$

The sphere diameter (careful: 2) has been previously measured and is given on the supply bottle. The density D is 1077 kg/m^3 (found by measuring a large batch of latex before it is made into little spheres).

Q9 What is the spacing between the observed average values of $1/V$ and what is the difference in charge that corresponds to this difference in $1/V$?

Q10 What is the smallest value of $1/V$ that you obtained? What is the corresponding value of q ?

Q11 Do your experimental results support the idea that electric charge is quantized? If so, what is *your value* for the quantum of charge?

Q12 If you have already measured q_e/m in Experiment 39, compute the mass of an electron. Even if your value differs the accepted value by a factor of 10, perhaps you will agree that its measurement is a considerable intellectual triumph.

EXPERIMENT 43 THE PHOTOELECTRIC EFFECT

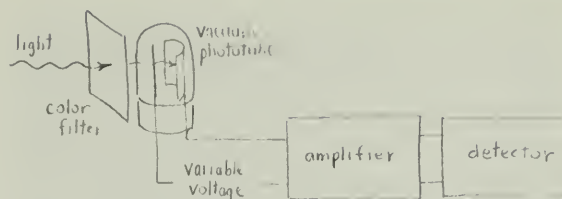
In this experiment you will make observations on the effect of light on a metal surface; then you will compare the appropriateness of the wave model and the particle model of light for explaining what you observe.

Before doing the experiment, read text Sec. 18.4 (Unit 5) on the photoelectric effect.

How the apparatus works

Light that you shine through the window of the phototube falls on a half-cylinder of metal called the emitter. The light drives electrons from the emitter surface.

Along the axis of the emitter (the center of the tube) is a wire called the collector. When the collector is made a few volts positive with respect to the emitter, practically all the emitted electrons are drawn to it, and will return to the emitter through an external wire. Even if the collector is made slightly negative, some electrons will reach it and there will be a measurable current in the external circuit.



However much the details may differ, any equipment for the photoelectric effect experiment will consist of these basic parts.

The small current can be amplified several thousand times and detected in any of several different ways. One way is to use a small loudspeaker in which the amplified photoelectric current causes an audible hum; another is to use a cathode ray oscilloscope. The following description assumes that the output current is read on a microammeter (Fig. 18-9).

The voltage control knob on the phototube unit allows you to vary the voltage between emitter and collector. In its full counter-clockwise position, the voltage is zero. As you turn the knob clockwise the "photocurrent" decreases. You are making the collector more

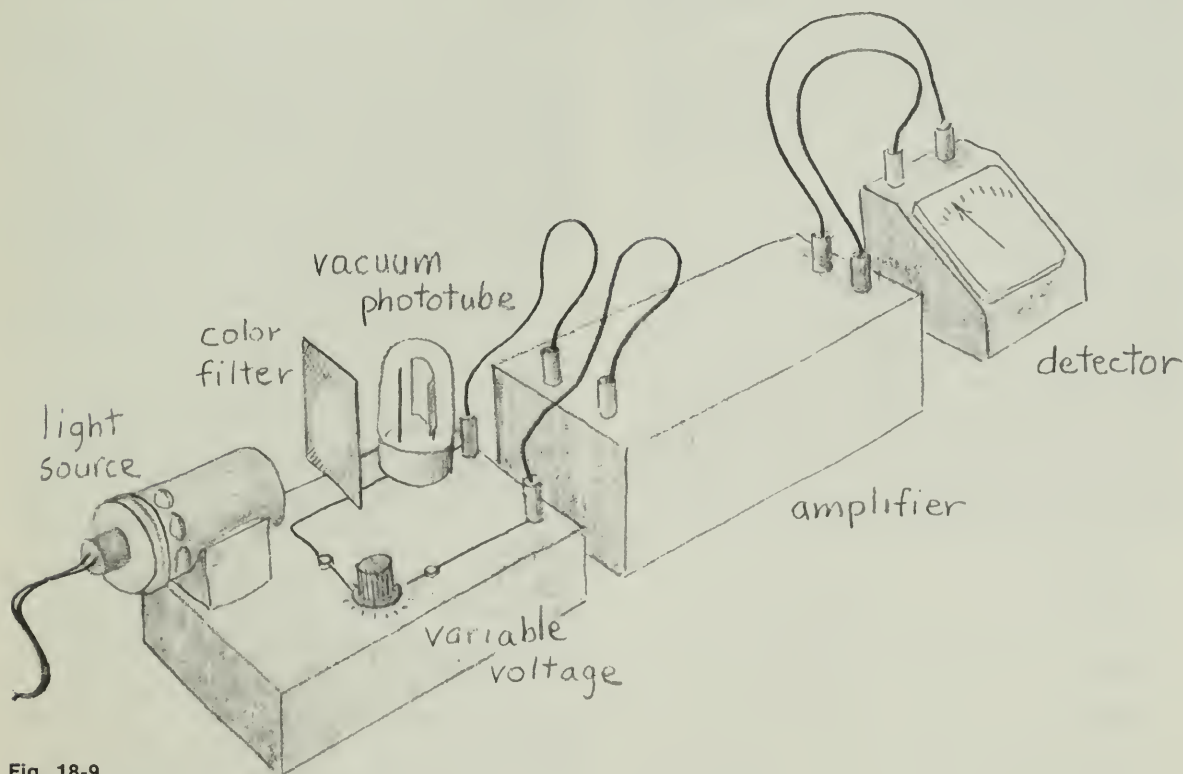


Fig. 18-9

and more negative and fewer and fewer electrons get to it. Finally the photocurrent ceases altogether—all the electrons are turned back before reaching the collector. The voltage between emitter and collector that just stops all the electrons is called the “stopping voltage.” The value of this voltage indicates the maximum kinetic energy with which the electrons leave the emitter. To find the value of the stopping voltage precisely you will have to be able to determine precisely when the photocurrent is reduced to zero. Because there is some drift of the amplifier output, the current indicated on the meter will drift around the zero point even when the actual current remains exactly zero. Therefore you will have to adjust the amplifier *offset* occasionally to be sure the zero level is really zero. An alternative is to ignore the precise reading of the current meter and adjust the collector voltage until *turning the light off and on causes no detectable change in the current*. Turn up the negative collector voltage until blocking the light from the tube (with black paper) has no effect on the meter reading—the exact location of the meter pointer isn’t important.

The position of the voltage control knob at the current cutoff gives you a rough measure of stopping voltage. To measure it more precisely, connect a voltmeter as shown in Fig. 18-10.

In the experiment you will measure the stopping voltages as light of different frequencies falls on the phototube. Good colored filters will allow light of only a certain range of frequencies to pass through. You can use a hand spectroscope to find the highest frequency line passed by each filter. The filters select frequencies from the mercury spectrum emitted by an intense mercury lamp. Useful frequencies of the mercury spectrum are:

Yellow	$5.2 \times 10^{14}/\text{sec}$
Green	$5.5 \times 10^{14}/\text{sec}$
Blue	$6.9 \times 10^{14}/\text{sec}$
Violet	$7.3 \times 10^{14}/\text{sec}$
(Ultraviolet)	$8.2 \times 10^{14}/\text{sec}$

DOING THE EXPERIMENT

Part I

The first part of the experiment is qualitative. To see if there is *time delay* between light falling on the emitter and the emission of photoelectrons, cover the phototube and then quickly remove the cover. Adjust the light source and filters to give the smallest photocurrent that you can conveniently notice on the meter.

Q1 Can you detect any time delay between the moment that light hits the phototube and the moment that motion of the microammeter pointer (or a hum in the loudspeaker or deflection of the oscilloscope trace) signals the passage of photoelectrons through the phototube?

To see if the *current* in the phototube depends on the intensity of incident light, vary the distance of the light source.

Q2 Does the *number* of photoelectrons emitted from the sensitive surface vary with light intensity—that is, does the output current of the amplifier vary with the intensity of the light?

To find out whether the *kinetic energy* of the photoelectrons depends on the *intensity* of the incident light, measure the stopping voltage with different intensities of light falling on the phototube.

Q3 Does the *kinetic energy* of the photoelectrons depend on *intensity*—that is, does the stopping voltage change?

Finally, determine how the *kinetic energy* of photoelectrons depends on the *frequency* of incident light. You will remember (Text Sec. 18.5) that the maximum kinetic energy of the photoelectrons is $V_{\text{stop}}q_e$, where V_{stop} is the stopping voltage and $q_e = 1.60 \times 10^{-19}$ coulombs, the charge on an electron. Measure the stopping voltage with various filters over the window.

Q4 How does the stopping voltage and hence the kinetic energy change as the light is changed from red through blue or ultraviolet (no filters)?

Part II

In the second part of the experiment you will

make more precise measurements of stopping voltage. To do this, adjust the voltage control knob to the cutoff (stopping voltage) position and then measure V with a voltmeter (Fig. 18-10.) Connect the voltmeter only after the cutoff adjustment is made so that the voltmeter leads will not pick up any ac voltage induced from other conducting wires in the room.

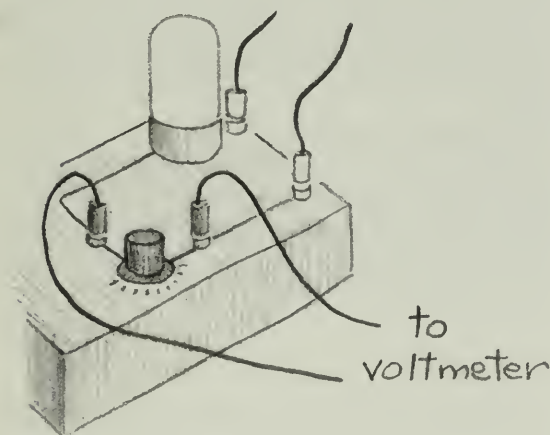


Fig. 18-10

Measure the stopping voltage V_{stop} for three or four different light frequencies, and plot the data on a graph. Along the vertical axis, plot electron energy $V_{stop}q_e$. When the stopping voltage V is in volts, and q_e is in coulombs, Vq_e will be energy, in joules.

Along the horizontal axis plot frequency of light f .

Interpretation of Results

As suggested in the opening paragraph, you can compare the wave model of light and the particle model in this experiment. Consider, then, how these models explain your observations.

Q5 If the light striking your phototube acts as *waves*—

- Can you explain why the stopping voltage should depend on the *frequency* of light?
- Would you expect the stopping voltage to depend on the *intensity* of the light? Why?
- Would you expect a delay between the time

that light first strikes the emitter and the emission of photoelectrons? Why?

Q6 If the light is acting as a stream of *particles*, what would be the answer to questions a, b and c above?

If you drew the graph suggested in the Part II of the experiment, you should now be prepared to interpret the graph. It is interesting to recall that Einstein predicted its form in 1905, and by experiments similar to yours, Millikan verified Einstein's prediction in 1916.

Einstein's photoelectric equation (Text Sec. 18.5) describes the energy of the most energetic photoelectrons (the last ones to be stopped as the voltage is increased), as

$$\begin{aligned}\frac{1}{2}mv_{max}^2 &= V_{stop}q_e \\ &= hf - W.\end{aligned}$$

This equation has the form

$$y = kx - c.$$

In this equation $-c$ is a constant, the value of y at the point where the straight line cuts the vertical axis; and k is another constant, namely the slope of the line. (See Fig. 18-11.) Therefore, the slope of a graph of $V_{stop}q_e$ against f should be h .

Q7 What is the value of the slope of *your* graph? How well does this value compare with

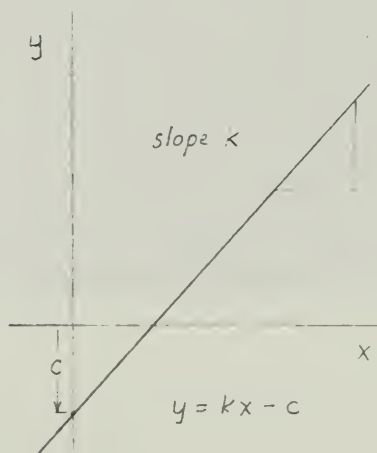


Fig. 18-11

the value of Planck's constant, $h = 6.6 \times 10^{-34}$ joule-sec? (See Fig. 18-12).

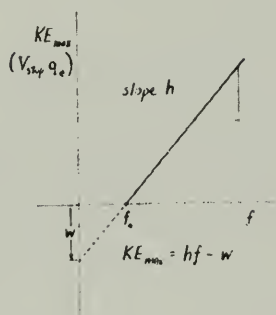


Fig. 18-12

With the equipment you used, the slope is unlikely to agree with the accepted value of h (6.6×10^{-34} joule-sec) more closely than an order of magnitude. Perhaps you can give a

few reasons why your agreement cannot be more approximate.

Q8 The lowest frequency at which any electrons are emitted from the cathode surface is called the *threshold frequency*, f_0 . At this frequency $\frac{1}{2}mv_{max} = 0$ and $hf_0 = W$, where W is the "work function." Your experimentally obtained value of W is not likely to be the same as that found for very clean cathode surfaces, more carefully filtered light, etc. The important thing to notice here is that there is a value of W , indicating that there is a minimum energy needed to release photoelectrons from the emitter.

Q9 Einstein's equation was derived from the assumption of a particle (photon) model of light. If your results do not fully agree with Einstein's equation, does this mean that your experiment supports the wave theory?

ACTIVITIES

WRITINGS BY OR ABOUT EINSTEIN

In addition to his scientific works, Einstein wrote many perceptive essays on other areas of life which are easy to read, and are still very current. The chapter titles from *Out of My Later Years* (Philosophical Library, N.Y. 1950) indicate the scope of these essays: Convictions and Beliefs; Science; Public Affairs; Science and Life; Personalities; My People. This book includes his writings from 1934 to 1950. *The World As I See It* includes material from 1922 to 1934. *Albert Einstein: Philosopher-Scientist*, Vol. I. (Harper Torchbook, 1959) contains Einstein's autobiographical notes, left-hand pages in German and right hand pages in English, and essays by twelve physicist contemporaries of Einstein about various aspects of his work. See also the three articles, "Einstein," "Outside and Inside the Elevator," and "Einstein and Some Civilized Discontents" in *Reader 5*.

MEASURING q/m FOR THE ELECTRON

With the help of a "tuning eye" tube such as you may have seen in radio sets, you can measure the charge-to-mass ratio of the electron in a way that is very close to J. J. Thomson's original method.

Complete instructions appear in the PSSC *Physics Laboratory Guide*, Second Edition, D. C. Heath Company, Experiment IV-12, "The Mass of the Electron," pp. 79-81.

CATHODE RAYS IN A CROOKES TUBE

A Crookes tube having a metal barrier inside it for demonstrating that cathode rays travel in straight lines may be available in your classroom. In use, the tube is excited by a Tesla coil or induction coil.

Use a Crookes tube to demonstrate to the class the deflection of cathode rays in magnetic fields. To show how a magnet focuses cathode rays, bring one pole of a strong bar magnet toward the shadow of the cross-shaped obstacle near the end of the tube. Watch what happens to the shadow as the magnet gets closer and closer to it. What happens when you

switch the poles of the magnet? What do you think would happen if you had a stronger magnet?

Can you demonstrate deflection by an electric field? Try using static charges as in Experiment 34, "Electric Forces I," to create a deflecting field. Then if you have an electrostatic generator, such as a small Van de Graaff or a Wimshurst machine, try deflecting the rays using parallel plates connected to the generator.

X RAYS FROM A CROOKES TUBE

To demonstrate that x rays penetrate materials that stop visible light, place a sheet of 4" \times 5" 3000-ASA-speed Polaroid Land film, still in its protective paper jacket, in contact with the end of the Crookes' tube. (A film pack cannot be used, but any other photographic film in a light-tight paper envelope could be substituted.) Support the film on books or the table so that it doesn't move during the exposure. Fig. 18-13 was a 1-minute exposure using a hand-held Tesla coil to excite the Crookes tube.



Fig. 18-13

LIGHTING AN ELECTRIC LAMP WITH A MATCH

Here is a trick with which you can challenge your friends. It illustrates one of the many amusing and useful applications of the photo-

electric effect in real life. You will need the phototube from Experiment 42, "The Photoelectric Effect," together with the Project Physics Amplifier and Power Supply. You will also need a $1\frac{1}{2}$ V dry cell or power supply and a 6V light source such as the one used in the Millikan Apparatus. (If you use this light source, remove the lens and cardboard tube and use only the 6V lamp.) Mount the lamp on the Photoelectric Effect apparatus and connect it to the 0-5V, 5 amps variable output on the power supply. Adjust the output to maximum. Set the *transistor switch input* switch to switch.

Connect the Photoelectric Effect apparatus to the Amplifier as shown in Fig. 18-14. Notice that the polarity of the 1.5V cell is reversed and that the output of the Amplifier is connected to the *transistor switch input*.

Advance the gain control of the amplifier to maximum, then adjust the offset control in a positive direction until the filament of the 6V lamp ceases to glow. Ignite a match near the apparatus (the wooden type works the best) and bring it quickly to the window of the phototube while the phosphor of the match is still glowing brightly. The phosphor flare of the match head will be bright enough to cause sufficient photocurrent to operate the transistor switch which turns the bulb on. Once the bulb is lit, it keeps the photocell activated by its own light; you can remove the match and the bulb will stay lit.

When you are demonstrating this effect, tell your audience that the bulb is really a candle and that it shouldn't surprise them that you can light it with a match. And of course one way to put out a candle is to moisten your fingers and pinch out the wick. When your fingers pass between the bulb and the photo-

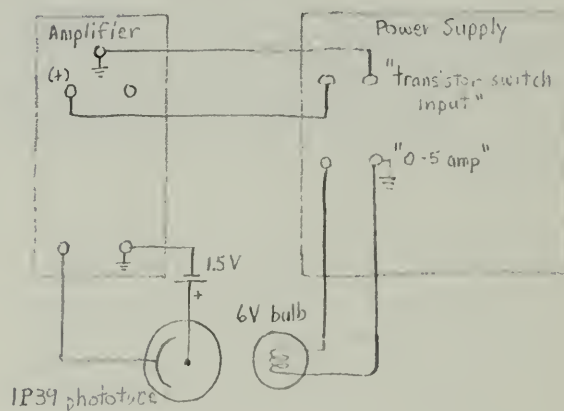
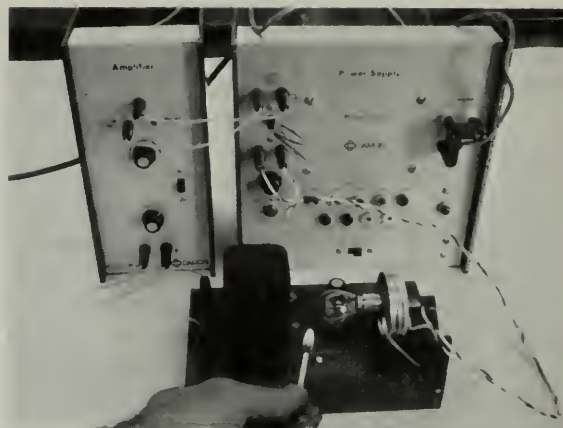


Fig. 18-14

cell, the bulb turns off, although the filament may glow a little, just as the wick of a freshly snuffed candle does. You can also make a "candle-snuffer" from a little cone of any reasonable opaque material and use this instead of your fingers. Or you can "blow out" the bulb: It will go out obediently if you take care to remove it from in front of the photocell as you blow it out.

FILM LOOP

FILM LOOP 47 THOMSON MODEL OF THE ATOM

Before the development of the Bohr theory, a popular model for atomic structure was the “raisin pudding” model of J. J. Thomson. According to this model, the atom was supposed to be a uniform sphere of positive charge in which were embedded small negative “corpuscles” (electrons). Under certain conditions the electrons could be detached and observed separately, as in Thomson’s historic experiment to measure the charge/mass ratio.

The Thomson model did not satisfactorily explain the stability of the electrons and especially their arrangement in “rings,” as suggested by the periodic table of the elements. In 1904 Thomson performed experiments which to him showed the *possibility* of a ring structure within the broad outline of the raisin-pudding model. Thomson also made mathematical calculations of the various arrangements of electrons in his model.

In the Thomson model of the atom, the cloud of positive charge created an electric field directed along radii, strongest at the surface of the sphere of charge and decreasing to zero at the center. You are familiar with a gravitational example of such a field. The earth’s downward gravitational field is strongest at the surface and it decreases uniformly toward the center of the earth.

For his model-of-a-model Thomson used still another type of field—a magnetic field caused by a strong electromagnet above a tub of water. Along the water surface the field is “radial,” as shown by the pattern of iron filings sprinkled on the glass bottom of the tub. Thomson used vertical magnetized steel needles to represent the electrons; these were stuck through corks and floated on the surface of the water. The needles were oriented with like poles pointing upward; their mutual repulsion tended to cause the magnets to spread apart. The outward repulsion was counteracted by the radial magnetic field directed inward toward the center. When the floating magnets were placed in the tub of water, they came to

equilibrium configurations under the combined action of all the forces. Thomson saw in this experiment a partial verification of his calculation of how electrons (raisins) might come to equilibrium in a spherical blob of positive fluid.

In the film the floating magnets are 3.8 cm long, supported by ping pong balls (Fig. 18-15). Equilibrium configurations are shown for various numbers of balls, from 1 to 12. Perhaps you can interpret the patterns in terms of rings, as did Thomson.



Fig. 18-15

Thomson was unable to make an exact correlation with the facts of chemistry. For example, he knew that the eleventh electron is easily removed (corresponding to sodium, the eleventh atom of the periodic table), yet his floating magnet model failed to show this. Instead, the patterns for 10, 11 and 12 floating magnets are rather similar.

Thomson’s work with this apparatus illustrates how physical theories may be tested with the aid of analogies. He was disappointed by the failure of the model to account for the details of atomic structure. A few years later the Rutherford model of a nuclear atom made the Thomson model obsolete, but in its day the Thomson model received some support from experiments such as those shown in the film.

Chapter 19 The Rutherford-Bohr Model of the Atom

EXPERIMENT 44 SPECTROSCOPY

In text Chapter 19 you learn of the immense importance of spectra to our understanding of nature. You are about to observe the spectra of a variety of light sources to see for yourself how spectra differ from each other and to learn how to measure the wavelengths of spectrum lines. In particular, you will measure the wavelengths of the hydrogen spectrum and relate them to the structure of the hydrogen atom.

Before you begin, review carefully Sec. 19.1 of text Chapter 19.

Creating spectra

Materials can be made to give off light (or be "excited") in several different ways: by heating in a flame, by an electric spark between electrodes made of the material, or by an electric current through a gas at low pressure.

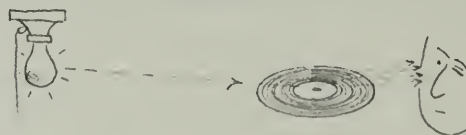
The light emitted can be dispersed into a spectrum by either a prism or a diffraction grating.

In this experiment, you will use a diffraction grating to examine light from various sources. A diffraction grating consists of many very fine parallel grooves on a piece of glass or plastic. The grooves can be seen under a 400-power microscope.

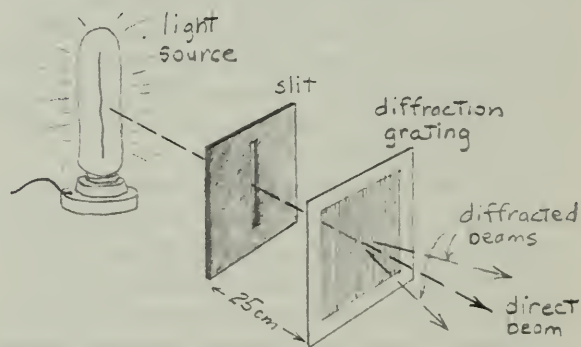
In experiment 33 (Young's Experiment) you saw how two narrow slits spread light of different wavelengths through different angles, and you used the double slit to make approximate measurements of the wavelengths of light of different colors. The distance between the two slits was about 0.2 mm. The distance between the lines in a diffraction grating is about 0.002 mm. And a grating may have about 10,000 grooves instead of just two. Because there are more lines and they are closer together, a grating diffracts more light and separates the different wavelengths more than a double-slit, and can be used to make very accurate measurements of wavelength.

Observing spectra

You can observe diffraction when you look at light that is reflected from a phonograph record. Hold the record so that light from a distant source is almost parallel to the record's surface, as in the sketch below. Like a diffraction grating, the grooved surface disperses light into a spectrum.



Use a real diffraction grating to see spectra simply by holding the grating close to your eye with the lines of the grating parallel to a distant light source. Better yet, arrange a slit about 25 cm in front of the grating, as shown below, or use a pocket spectroscope.



Look through the pocket spectroscope at a fluorescent light, at an ordinary (incandescent) light bulb, at mercury-vapor and sodium-vapor street lamps, at neon signs, at light from the sky (but *don't* look directly at the sun), and at a flame into which various compounds are introduced (such as salts of sodium, potassium, strontium, barium, and calcium).

Q1 Which color does the grating diffract into the widest angle and which into the narrowest? Are the long wavelengths diffracted at a

wider angle than the short wavelengths, or vice-versa?

Q2 The spectra discussed in the *Text* are (a) either emission or absorption, and (b) either line or continuous. What different *kinds* of spectra have you observed? Make a table showing the type of spectrums produced by each of the light sources you observed. Do you detect any relationship between the nature of the source and the kind of spectra it produces?

Photographing the spectrum

A photograph of a spectrum has several advantages over visual observation. A photograph reveals a greater range of wavelengths; also it allows greater convenience for your measurement of wavelengths.

When you hold the grating up to your eye, the lens of your eye focuses the diffracted rays to form a series of colored images on the retina. If you put the grating in front of the camera lens (focused on the source), the lens will produce sharp images on the film.

The spectrum of hydrogen is particularly interesting to measure because hydrogen is the simplest atom and its spectrum is fairly easily related to a model of its structure. In this experiment, hydrogen gas in a glass tube is excited by an electric current. The electric discharge separates most of the H_2 molecules into single hydrogen atoms.)

Set up a meter stick just behind the tube (Fig. 19-1). This is a scale against which to observe and measure the position of the spectrum lines. The tube should be placed at about the 70-cm mark since the spectrum viewed through the grating will appear nearly 70 cm long.

From the camera position, look through the grating at the glowing tube to locate the positions of the visible spectral lines against the meter stick. Then, with the grating fastened over the camera lens, set up the camera with its lens in the same position your eye was. The lens should be aimed perpendicularly at the 50 cm mark, and the grating lines must be parallel to the source.

Now take a photograph that shows both the scale on the meter stick and the spectral



Fig. 19-1

lines. You may be able to take a single exposure for both, or you may have to make a double exposure—first the spectrum, and then, with more light in the room, the scale. It depends on the amount of light in the room. Consult your teacher.

Analyzing the spectrum

Count the number of spectral lines on the photograph, using a magnifier to help pick out the faint ones.

Q3 Are there more lines than you can see when you hold the grating up to your eye? If you do see additional lines, are they located in the visible part of the spectrum (between red and violet) or in the infrared or ultraviolet part?

The angle θ through which light is diffracted by a grating depends on the wavelength λ of the light and the distance d between lines on the grating. The formula is a simple one:

$$\lambda = d \sin \theta.$$

To find θ , you need to find $\tan \theta = x/l$ as shown in Fig. 19-2. Here x is the distance of the spectral line along the meter stick from the source, and l is the distance from the source to the grating. Use a magnifier to read x from your photograph. Calculate $\tan \theta$, and then look up the corresponding values of θ and $\sin \theta$ in trigonometric tables.

To find d , remember that the grating space is probably given as lines per inch. You must convert this to the distance between lines in meters. One inch is 2.54×10^{-2} meters, so if there are 13,400 lines per inch, then d is

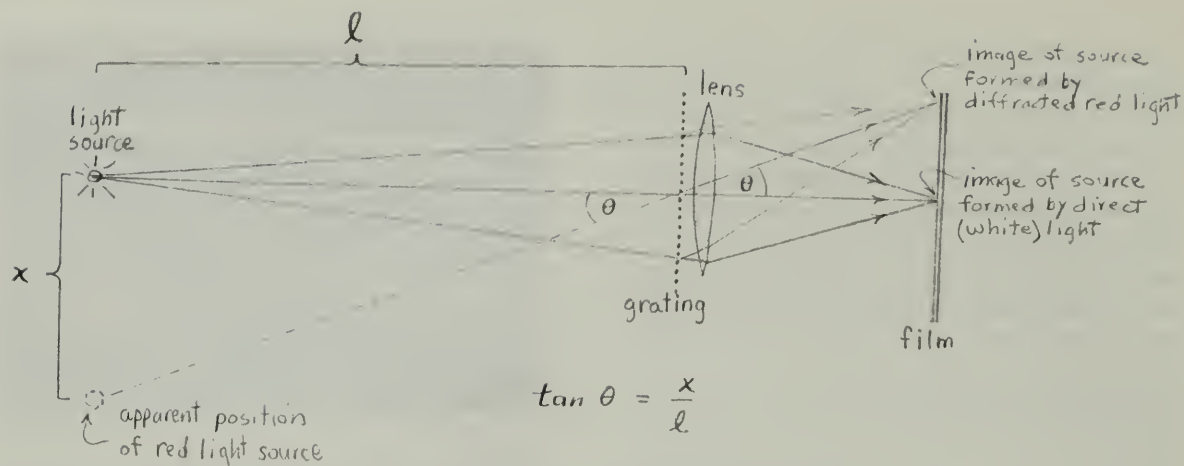


Fig. 19-2 Different images of the source are formed on the film by different colors of diffracted light. The angle of diffraction is equal to the apparent angular displacement angle of the source in the photograph so

$$\tan \theta = \frac{x}{l}$$

$$(2.54 \times 10^{-2}) / (1.34 \times 10^4) = 1.89 \times 10^{-6} \text{ meters.}$$

Calculate the values of λ for the various spectral lines you have measured.

Q4 How many of these lines are visible to the eye?

Q5 What would you say is the shortest wave length to which your eye is sensitive?

Q6 What is the shortest wavelength that you can measure on the photograph?

Compare your values for the wavelengths with those given in the text, or in a more complete list (for instance, in the *Handbook of Chemistry and Physics*). The differences between your values and the published ones should be less than the experimental uncertainty of your measurement. Are they?

This is not all that you can do with the results of this experiment. You could, for example, work out a value for the Rydberg constant for hydrogen (mentioned in Text Sec. 19.2).

More interesting perhaps is to calculate some of the energy levels for the excited hydrogen atom. Using Planck's constant ($h = 6.6 \times 10^{-34}$), the speed of light in vacuum ($c = 3.0 \times 10^8$ m/sec), and your measured value of the wavelength λ of the separate lines, you can calculate the energy of photons' various wavelengths, $E = hf = hc/\lambda$ emitted when hydrogen atoms change from one state to another. The energy of the emitted photon is the difference in energy between the initial and final states

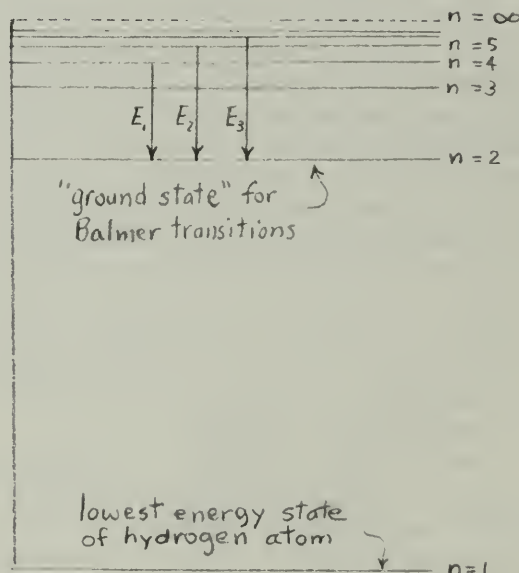


Fig. 19-3 of the atom.

Make the assumption (which is correct) that for all lines of the series you have observed the final energy state is the same. The energies that you have calculated represent the energy of various excited states above this final level.

Draw an energy-level diagram something like the one shown here (Fig. 19-3). Show on it the energy of the photon emitted in transition from each of the excited states to the final state.

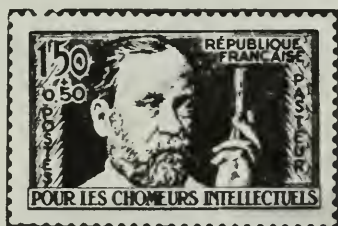
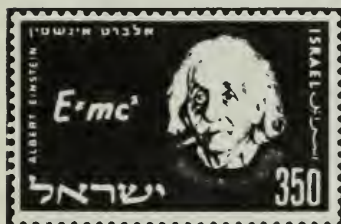
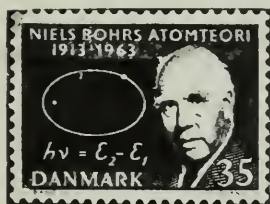
Q7 How much energy does an excited hydrogen atom lose when it emits red light?

ACTIVITIES

SCIENTISTS ON STAMPS

As shown here, scientists are pictured on the stamps of many countries, often being honored by other than their homeland. You may want to visit a stamp shop and assemble a display for your classroom.

See also "Science and the Artist," in the Unit 4 *Handbook*.



MEASURING IONIZATION, A QUANTUM EFFECT

With an inexpensive thyratron 885 tube, you can demonstrate an effect that is closely related to the famous Franck-Hertz effect.

Theory

According to the Rutherford-Bohr model, an atom can absorb and emit energy only in certain amounts that correspond to permitted "jumps" between states.

If you keep adding energy in larger and larger "packages," you will finally reach an amount large enough to separate an electron entirely from its atom—that is, to ionize the atom. The energy needed to do this is called the *ionization energy*.

Now imagine a beam of electrons being accelerated by an electric field through a region of space filled with argon atoms. This is the situation in a thyratron 884 tube with its grid and anode both connected to a source of variable voltage, as shown schematically in Fig. 19-4).

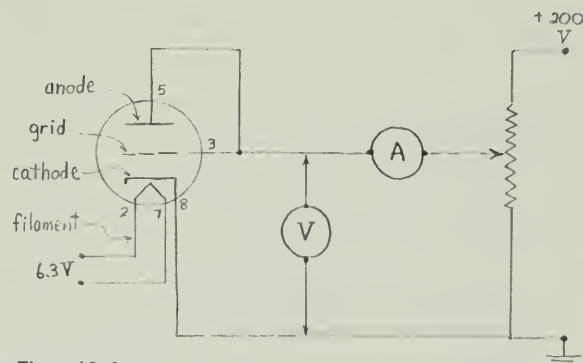


Fig. 19-4

In the form of its kinetic energy each electron in the beam carries energy in a single "package." The electrons in the beam collide with argon atoms. As you increase the accelerating voltage, the electrons eventually become energetic enough to excite the atoms, as in the Franck-Hertz effect. However, your equipment is not sensitive enough to detect the resulting small energy absorptions. So nothing seems to happen. The electron current from cathode to anode appears to increase quite linearly with the voltage, as you would expect—until the

electrons get up to the ionization energy of argon. This happens at the *ionization potential* V_i , which is related to the ionization energy E_i and to the charge q_e on the electron as follows:

$$E_i = q_e V_i$$

As soon as electrons begin to ionize argon atoms, the current increases sharply. The argon is now in a different state, called an ionized state, in which it conducts electric current much more easily than before. Because of this sudden decrease in electrical resistance, we may use the thyratron tube as an “electronic switch” in such devices as stroboscopes. (A similar process ionizes the air so that it can conduct lightning.) As argon ions recapture electrons, they emit photons of ultraviolet and of visible violet light. When you see this violet glow, the argon gas is being ionized.

For theoretical purposes, the important point is that ionization takes place in any gas at a particular energy that is characteristic of that gas. This is easily observed evidence of one special case of Bohr’s postulated discrete energy states.

Equipment

Thyratron 884 tube
Octal socket to hold the tube (not essential but convenient)
Voltmeter (0-30 volts dc)
Ammeter (0-100 milliamperes)
Potentiometer (10,000 ohm, 2 watts or larger) or variable transformer, 0-120 volts ac
Power supply, capable of delivering 50-60 mA at 200 volts dc
Connect the apparatus as shown schematically in Fig. 19-7.

Procedure

With the potentiometer set for the lowest available anode voltage, turn on the power and wait a few seconds for the filament to heat. Now increase the voltage by small steps. At each new voltage, call out to your partner the voltmeter reading. Pause only long enough to permit your partner to read the ammeter and to note both

readings in your data table. Take data as rapidly as accuracy permits: Your potentiometer will heat up quickly, especially at high currents. If it gets too hot to touch, turn the power off and wait for it to cool before beginning again.

Watch for the onset of the violet glow. Note in your data table the voltage at which you first observe the glow, and then note what happens to the glow at higher voltages.

Plot current versus voltage, and mark the point on your graph where the glow first appeared. From your graph, determine the first ionization potential of argon. Compare your experimental value with published values, such as the one in the *Handbook of Chemistry and Physics*.

What is the energy an electron must have in order to ionize an argon atom?

MODELING ATOMS WITH MAGNETS

Here is one easy way to demonstrate some of the important differences between the Thomson “raisin pudding” atom model and the Rutherford nuclear model.

To show how alpha particles would be expected to behave in collisions with a Thomson atom, represent the spread-out “pudding” of positive charge by a roughly circular arrangement of small disc magnets, spaced four or five inches apart, under the center of a smooth tray, as shown in Fig. 19-5. Use tape



Fig. 19-5 The arrangement of the magnets for a “Thomson atom”.

or putty to fasten the magnets to the underside of the tray. Put the large magnet (representing the alpha particle) down on top of the tray in such a way that the large magnet is repelled by the small magnets and sprinkle onto the tray enough tiny plastic beads to make the large magnet slide freely. Now push the “alpha particle” from the edge of the tray toward the “atom.” As long as the “alpha particle” has enough momentum to reach the other side, its deflection by the small magnets under the tray will be quite small—never more than a few degrees.

For the Rutherford model, on the other hand, gather all the small magnets into a vertical stack under the center of the tray, as shown in Fig. 19-6. Turn the stack so that it



Fig. 19-6 The arrangement of the magnets for a “Rutherford atom.”

repels “alpha particles” as before. This “nucleus of positive charge” now has a much greater effect on the path of the “alpha particle.”

Have a partner tape an unknown array of magnets to the bottom of the tray—can you determine what it is like just by scattering the large magnet?

With this magnet analogue you can do some quantitative work with the scattering relationships that Rutherford investigated. (See text Sec. 19.3 and Film Loop 48, “Rutherford Scattering” at the end of this *Handbook* chapter.) Try again with different sizes of magnets. Devise a launcher so that you can control the velocity of your projectile magnets and the distance of closest approach.

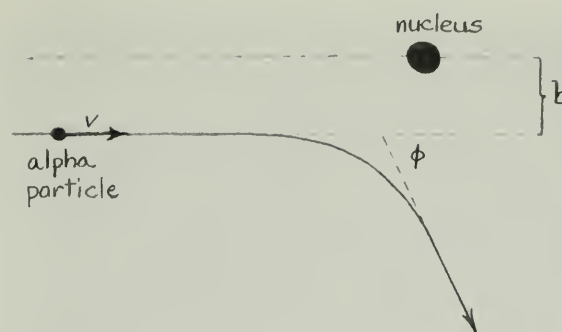


Fig. 19-7

- 1) Keep the initial projectile velocity v constant and vary the distance b (see Fig. 19-7); then plot the scattering angle ϕ versus b .
- 2) Hold b constant and carry the speed of the projectile, then plot ϕ versus v .
- 3) Try scattering hard, nonmagnetized discs off each other. Plot ϕ versus b and ϕ versus v as before. Contrast the two kinds of scattering-angle distributions.

“BLACK BOX” ATOMS

Place two or three different objects, such as a battery, a small block of wood, a bar magnet, or a ball bearing, in a small box. Seal the box, and have one of your fellow students try to tell you as much about the contents as possible, without opening the box. For example, sizes might be determined by tilting the box, relative masses by balancing the box on a support, or whether or not the contents are magnetic by checking with a compass.

The object of all this is to get a feeling for what you can or cannot infer about the structure of an atom purely on the basis of secondary evidence. It may help you to write a report on your investigation in the form you may have used for writing a proof in plane geometry, with the property of the box in one column and your reason for asserting that the property is present in the other column. The analogy can be made even better if you are exceptionally brave: Don't let the guesser open the box, ever, to find out what is really inside.

**ANOTHER SIMULATION
OF THE RUTHERFORD ATOM**

A hard rubber "potential-energy hill" is available from Stark Electronics Instruments, Ltd., Box 670, Ajax, Ontario, Canada. When you roll steel balls onto this hill, they are deflected in

somewhat the same way as alpha particles are deflected away from a nucleus. The potential-energy hill is very good for quantitative work such as that suggested for the magnet analogue in the activity "Modeling atoms with magnets."

FILM LOOPS

FILM LOOP 48: RUTHERFORD SCATTERING

This film simulates the scattering of alpha particles by a heavy nucleus, such as gold, as in Ernest Rutherford's famous experiment. The film was made with a digital computer.

The computer program was a slight modification of that used in film loops 13 and 14, on program orbits, concerned with planetary orbits. The only difference is that the operator selected an inverse-square law of *repulsion* instead of a law of attraction such as that of gravity. The results of the computer calculation were displayed on a cathode-ray tube and then photographed. Points are shown at equal time intervals. Verify the law of areas for the motion of the alpha particles by projecting the film for measurements. Why would you expect equal areas to be swept out in equal times?

All the scattering particles shown are near a nucleus. If the image from your projector is 1 foot high, the nearest adjacent nucleus would be about 500 feet above the nucleus shown. Any alpha particles moving through this large area between nuclei would show no appreciable deflection.

We use the computer and a mathematical model to tell us what the result will be if we shoot particles at a nucleus. The computer does not "know" about Rutherford scattering. What it does is determined by a program placed in the computer's memory, written in this particular instance in a language called Fortran. The programmer has used Newton's laws of motion and has assumed an inverse-square repulsive force. It would be easy to change the program to test another force law, for ex-



ample $F = K/r^3$. The scattering would be computed and displayed; the angle of deflection for the same distance of closest approach would be different than for inverse-square force.

Working backward from the observed scattering data, Rutherford deduced that the inverse-square Coulomb force law is correct for all motions taking place at distances greater than about 10^{-14}m from the scattering center, but he found deviations from Coulomb's law for closer distances. This suggested a new type of force, called nuclear force. Rutherford's scattering experiment showed the size of the nucleus (supposedly the same as the range of the nuclear forces) to be about 10^{-14}m , which is about 1/10,000 the distance between the nuclei in solid bodies.

Chapter 20 Some Ideas from Modern Physical Theories

ACTIVITIES

STANDING WAVES ON A BAND-SAW BLADE

Standing waves on a ring can be shown by shaking a band-saw blade with your hand. Wrap tape around the blade for about six inches to protect your hand. Then gently shake the blade up and down until you have a feeling for the lowest vibration rate that produces reinforcement of the vibration. Then double the rate of shaking, and continue to increase the rate of shaking, watching for standing waves. You should be able to maintain five or six nodes.

TURNTABLE OSCILLATOR PATTERNS RESEMBLING DE BROGLIE WAVES

If you set up two turntable oscillators and a Variac as shown in Fig. 20-1, you can draw pictures resembling de Broglie waves, like those shown in Chapter 20 of your text.

Place a paper disc on the turntable. Set both turntables at their lowest speeds. Before starting to draw, check the back-and-forth motion of the second turntable to be sure the pen stays on the paper. Turn both turntables on and use the Variac as a precise speed control on the second turntable. Your goal is to get the pen to follow exactly the same path each time the paper disc goes around. Try higher frequencies of back-and-forth motion to get more wavelengths around the circle.

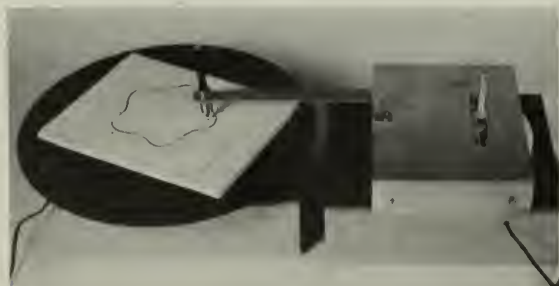


Fig. 20-1

For each stationary pattern that you get, check whether the back-and-forth frequency is an integral multiple of the circular frequency.

STANDING WAVES IN A WIRE RING

With the apparatus described below, you can set up circular waves that somewhat resemble the de Broglie wave models of certain electron orbits. You will need a strong magnet, a fairly stiff wire loop, a low-frequency oscillator, and a power supply with a transistor chopping switch.

The output current of the oscillator is much too small to interact with the magnetic field enough to set up visible standing waves in the wire ring. However, the oscillator current can operate the transistor switch to control ("chop") a much larger current from the power supply (see Fig. 20-2).

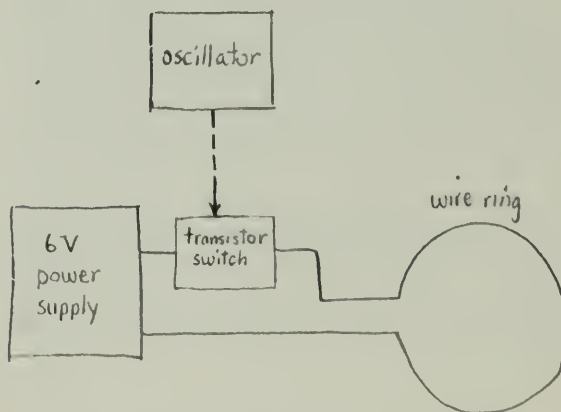


Fig. 20-2 The signal from the oscillator controls the transistor switch, causing it to turn the current from the power supply on and off. The "chopped" current in the wire ring interacts with the magnetic field to produce a pulsating force on the wire.

The wire ring must be of non-magnetic metal. Insulated copper magnet wire works well: Twist the ends together and support the

ring at the twisted portion by means of a binding post, Fahnestock clip, thumbtack, or ring-stand clamp. Remove a little insulation from each end for electrical connections.

A ring 4 to 6 inches in diameter made of 22-gauge enameled copper wire has its lowest rate of vibration at about 20 cycles/sec. Stiffer wire or a smaller ring will have higher characteristic vibrations that are more difficult to see.

Position the ring as shown, with a section of the wire passing between the poles of the magnet. When the pulsed current passes through the ring, the current interacts with the magnetic field, producing alternating forces which cause the wire to vibrate. In Fig. 20-2, the magnetic field is vertical, and the vibrations are in the plane of the ring. You can turn the magnet so that the vibrations are perpendicular to the ring.

Because the ring is clamped at one point, it can support standing waves that have any integral number of half wavelengths. In this respect they are different from waves on a *free* wire ring, which are restricted to integral numbers of *whole* wavelengths. Such waves are more appropriate for comparison to an atom.

When you are looking for a certain mode of vibration, position the magnet between expected nodes (at antinodes). The first "characteristic, or state" "mode of vibration," that the ring can support in its plane is the first harmonic, having two nodes: the one at the point

of support and the other opposite it. In the second mode, three nodes are spaced evenly around the loop, and the best position for the magnet is directly opposite the support, as shown in Fig. 20-3.

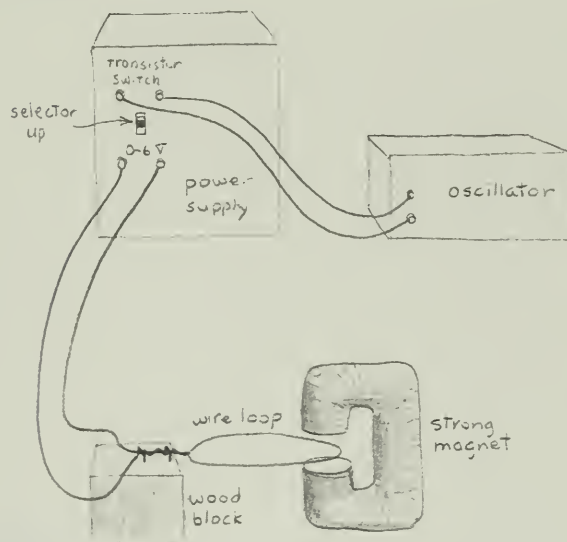


Fig. 20-3

You can demonstrate the various modes of vibration to the class by setting up the magnet, ring, and support on the platform of an overhead projector. Be careful not to break the glass with the magnet, especially if the frame of the projector happens to be made of a magnetic material.

The Project Physics *Film Loop* "Vibrations of a Wire," also shows this.

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Answers to End-of-Section Questions

Chapter 17

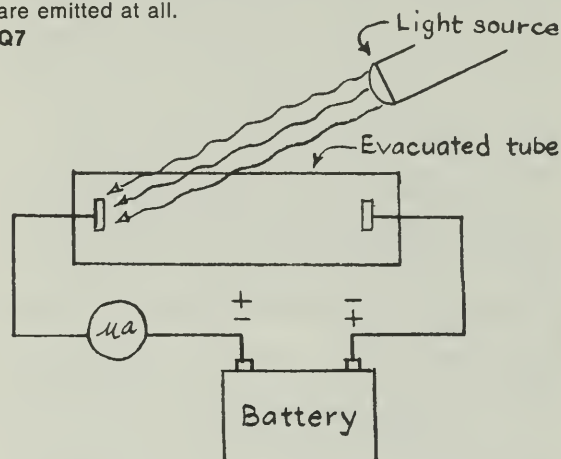
- Q1** The atoms of any one element are identical and unchanging.
- Q2** Conservation of matter; the constant ratio of combining weights of elements. These successes lend strength to the atomic theory of matter and to the hypothesis that chemical elements differ from one another because they are composed of different kinds of atoms.
- Q3** No.
- Q4** It was the lightest known element—and others were rough multiples.
- Q5** Relative mass; and combining number, or "valence."
- Q6** 2, 4, 5, 1, 2.
- Q7** Density, melting point, chemical activity, "valence."
- Q8** Because when the elements are arranged as they were in his table, there is a *periodic* recurrence of elements with similar properties; that is, elements with similar properties tend to fall in the same column of the table.
- Q9** Increasing atomic mass.
- Q10** When he found that the chemical properties of the next heaviest element clearly indicated that it did not belong in the next column but in one further to the right.
- Q11** He was able to predict in considerable detail the properties of missing elements, and these predictions proved to be extremely accurate, once the missing elements were discovered and studied.
- Q12** Its position in the periodic table, determined by many properties but usually increasing regularly with atomic mass. Some examples are: hydrogen, 1; oxygen, 8; uranium, 92.
- Q13** Water, which had always been considered a basic element, and had resisted all efforts at decomposition, was easily decomposed.
- Q14** New metals were separated from substances which had never been decomposed before.
- Q15** The amount of charge transferred by the current, the valence of the elements, and the atomic mass of the element.
- Q16** First, when two elements combine, the ratio of their combining masses is equal to the ratio of their values for A/v . Secondly, A/v is a measure of the amount of the material which will be deposited in electrolysis.

Chapter 18

- Q1** They could be deflected by magnetic and electric fields.
- Q2** The mass of an electron is about 1800 times smaller than the mass of a hydrogen ion.
- Q3** (1) Identical electrons were emitted by a variety of materials; and (2) the mass of an electron was much smaller than that of an atom.
- Q4** All other values of charge he found were multiples of that lowest value.
- Q5** Fewer electrons are emitted, but with the same average energy as before.

- Q6** The average kinetic energy of the emitted electrons decreases until, below some frequency value, none are emitted at all.

Q7



- Q8** The energy of the quantum is proportional to the frequency of the wave, $E = hf$.
- Q9** The electron loses some kinetic energy in escaping from the surface.
- Q10** The maximum kinetic energy of emitted electrons is 2.0 eV.
- Q11** When x rays passed through material, say air, they caused electrons to be ejected from molecules, and so produced $+$ ions.
- Q12** (1) Not deflected by magnetic field; (2) show diffraction patterns when passing through crystals; (3) produced a pronounced photoelectric effect.
- Q13** (1) Diffraction pattern formed by "slits" with atomic spacing (that is, crystals); (2) energy of quantum in photoelectric effect; (3) their great penetrating power.
- Q14** For atoms to be electrically neutral, they must contain enough positive charge to balance the negative charge of the electrons they contain; but electrons are thousands of times lighter than atoms.
- Q15** There are at least two reasons: First, the facts *never* are all in, so models cannot wait that long. Secondly, it is one of the main functions of a model to suggest what some of the facts (as yet undiscovered) might be.

Chapter 19

- Q1** The source emits light of only certain frequencies, and is therefore probably an excited gas.
- Q2** The source is probably made up of two parts: an inside part that produces a continuous spectrum; and an outer layer that absorbs only certain frequencies.
- Q3** Light from very distant stars produces spectra which are identical with those produced by elements and compounds here on earth.
- Q4** None (he predicted that they would exist because the mathematics was so neat).
- Q5** Careful measurement and tabulation of data on spectral lines, together with a liking for mathematical games.

Q6 At this point in the development of the book, one cannot say what specifically accounts for the correctness of Balmer's formula (the explanation requires atomic theory which is yet to come). But the success of the formula does indicate that there must be something about the structure of the atom which makes it emit only discrete frequencies of light.

Q7 They have a positive electric charge and are repelled by the positive electric charge in atoms. The angle of scattering is usually small because the nuclei are so tiny that the alpha particle rarely gets near enough to be deflected much. However, once in a while there is a close approach, and then the forces of repulsion are great enough to deflect the alpha particle through a large angle.

Q8 Rutherford's model located the positively charged bulk of the atom in a tiny nucleus—in Thomson's model the positive bulk filled the entire atom.

Q9 It is the number, Z , of positive units of charge found in the nucleus, or the number of electrons around the nucleus.

Q10 3 positive units of charge (when all 3 electrons were removed).

Q11 Atoms of a gas emit light of only certain frequencies, which implies that each atom's energy can change only by certain amounts.

Q12 None. (He *assumed* that electron orbits could have only certain values of angular momentum, which implied only certain energy states.)

Q13 All hydrogen atoms have the same size because in all unexcited atoms the electron is in the innermost allowable orbit.

Q14 The quantization of the orbits prevents them from having other arbitrary sizes.

Q15 Bohr *derived* his prediction from a physical model, from which other predictions could be made. Balmer only followed out a mathematical analogy.

Q16 According to Bohr's model, an absorption line would result from a transition within the atom from a lower to a higher energy state (the energy being absorbed from the radiation passing through the material).

Q17 (a) 4.0 eV (b) 0.1 eV (c) 2.1 eV.

Q18 The electron arrangements in noble gases are very stable. When an additional nuclear charge and an additional electron are added, the added electron is bound very weakly to the atom.

Q19 Period I contains the elements with electrons in the K shell only. Since only two electrons can exist in the

K shell, Period I will contain only the two elements with one electron and two electrons respectively. Period II elements have electrons in the K (full) and L shells. The L shell can accommodate 8 electrons, so those elements with only one through eight electrons in the L shell will be in Period II. And so forth.

Q20 It predicted some results that disagreed with experiment; and it predicted others which could not be tested in any known way. It did, however, give a satisfactory explanation of the observed frequency of the hydrogen spectral lines, and it provided a first physical picture of the quantum states of atoms.

Chapter 20

Q1 It increases, without limit.

Q2 It increases, approaching ever nearer to a limiting value, the speed of light.

Q3 Photon momentum is directly proportional to the frequency of the associated wave.

Q4 The Compton effect is the scattering of light (or x-ray) photons from electrons in such a way that the photons transfer a part of their energy and momentum to the electrons, and thus emerge as lower frequency radiation. It demonstrated that photons resemble material particles in possessing momentum as well as energy; both energy and momentum are conserved in collisions involving photons and electrons.

Q5 By analogy with the same relation for photons.

Q6 The regular spacing of atoms in crystals is about the same as the wavelength of low-energy electrons.

Q7 Bohr invented his postulate just for the purpose. Schrödinger's equation was derived from the wave nature of electrons and explained many phenomena other than hydrogen spectra.

Q8 It is almost entirely mathematical—no physical picture or models can be made of it.

Q9 It can. But less energetic photons have longer associated wavelengths, so that the location of the particle becomes less precise.

Q10 It can. But the more energetic photons will disturb the particle more and make measurement of velocity less precise.

Q11 They are regions where there is a high probability of quanta arriving.

Q12 As with all probability laws, the *average* behavior of a large collection of particles can be predicted with great precision.

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Brief Answers to Study Guide Questions

Chapter 17

- 17.1** Information
17.2 80.3% zinc; 19.7% oxygen
17.3 47.9% zinc
17.4 13.9 times mass of H atom; same
17.5 986 grams nitrogen; 214 grams hydrogen
17.6 9.23 times mass of H atom
17.7 (a) 14.1
(b) 28.2
(c) 7.0
17.8 Derivation
17.9 Na; 1 Al; 3 P; 5 Ca; 2 Sn; 4
17.10 (a) Ar—K; Co—Ni; Te—I; Th—Pa; U—Np;
Es—Fm; Md—No
(b) Discussion
17.11 Graph
17.12 Graph; discussion
17.13 8.0 grams; 0.895 gram
17.14 (a) 0.05 gram Zn
(b) 0.30 gram Zn
(c) 1.2 gram Zn
17.15 (a) 0.88 gram Cl
(b) 3.14 grams I
(c) Discussion
(d) Discussion
17.16 Discussion
17.17 Discussion
17.18 Discussion
17.19 35.45 grams
17.20 Discussion
17.21 Discussion
17.22 1, 3, 5
2, 4

Chapter 18

- 18.1** Information
18.2 (a) 2.0×10^7 m/sec
(b) 1.8×10^{11} coul/kg
18.3 Proof
18.4 Discussion
18.5 Discussion
18.6 2000 Å; ultraviolet
18.7 4×10^{-19} joule; 4×10^{-18} joule
18.8 2.6×10^{-19} ; 1.6 eV
18.9 4.9×10^{14} /sec
18.10 (a) 6×10^{14} /sec
(b) 4×10^{-19} joule
(c) 2.5×10^{20} photons
(d) 2.5 photons/sec
(e) 0.4 sec
(f) 2.5×10^{-10} photon
(g) 6.25×10^{17} electrons/sec; 0.1 amp
18.11 1.3×10^{17} photons
18.12 (a) 6.0×10^{23} electrons
(b) 84×10^{21} copper atoms/cm³
(c) 1.2×10^{-23} cm³
(d) 2.3×10^{-3} cm
18.13 (a) $2x = n\lambda$
(b) $2x = \text{any odd number of half wavelengths}$
(c) $\cos \theta = 2d/\lambda$ for first order
18.14 1.2×10^{19} /sec
18.15 Discussion
18.16 1.2×10^5 volts; 1.9×10^{-14} joule; 1.2×10^5 eV
18.17 Glossary
18.18 Discussion

Chapter 19

- 19.1 Information
- 19.2 Discussion
- 19.3 Five listed in Text, but theoretically an infinite number.
Four lines in visible region.
- 19.4 $n = 8$; $\lambda = 3880 \text{ \AA}$
 $n = 10$; $\lambda = 3790 \text{ \AA}$
 $n = 12$; $\lambda = 3740 \text{ \AA}$
- 19.5 (a) Yes
(b) $n_i = \infty$
(c) Lyman series 910 \AA ; Balmer series 3650 \AA ;
Paschen series 8200 \AA
(d) $21.8 \times 10^{-19} \text{ joule}$, 13.6 eV
- 19.6 Discussion
- 19.7 Discussion
- 19.8 $2.6 \times 10^{-14} \text{ m}$
- 19.9 (a) Discussion
(b) $10^{-4}/1$
- 19.10 3.5 m
- 19.11 Derivation
- 19.12 Discussion
- 19.13 List
- 19.14 Diagram
- 19.15 Discussion
- 19.16 Discussion
- 19.17 Discussion
- 19.18 Discussion
- 19.19 Discussion
- 19.20 Discussion
- 19.21 Discussion
- 19.22 Essay
- 19.23 Discussion

Chapter 20

- 20.1 Information
- 20.2 0.14 c or $4.2 \times 10^7 \text{ m/sec}$
- 20.3 $3.7 \times 10^{-14} \text{ newtons}$
- 20.4 $p = m_0 v$ and $KE = m_0 v^2/2$
- 20.5 (a) Changes are too small
(b) $1.1 \times 10^{-12} \text{ kg}$
- 20.6 (a) $2.7 \times 10^{33} \text{ joules}$
(b) $3.0 \times 10^{16} \text{ kg}$
(c) $5 \times 10^{-7} \%$
(d) Rest mass
- 20.7 (a) $1.2 \times 10^{-22} \text{ kg} \cdot \text{m/sec}$
(b) $1.1 \times 10^{-22} \text{ kg} \cdot \text{m/sec}$
(c) $2.4 \times 10^{-22} \text{ kg} \cdot \text{m/sec}$
(d) $1.1 \times 10^{-22} \text{ kg} \cdot \text{m/sec}$
- 20.8 $p = 1.7 \times 10^{-27} \text{ kg} \cdot \text{m/sec}$; $v = 1.9 \times 10^3 \text{ m/sec}$
- 20.9 Discussion
- 20.10 Diagram
- 20.11 $6.6 \times 10^6 \text{ m/sec}$
- 20.12 $3.3 \times 10^{-33} \text{ m}$
- 20.13 λ becomes larger
- 20.14 Discussion
- 20.15 $3 \times 10^{-31} \text{ m}$
- 20.16 Discussion
- 20.17 (a) $3.3 \times 10^{-25} \text{ m/sec}$
(b) $5.0 \times 10^{-8} \text{ m/sec}$
(c) $3.3 \times 10^{-6} \text{ m/sec}$
(d) $3.3 \times 10^6 \text{ m/sec}$
- 20.18 Discussion
- 20.19 Discussion
- 20.20 Discussion
- 20.21 Discussion
- 20.22 Discussion
- 20.23 Discussion
- 20.24 Discussion

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